







## **THE SOIL SOLUTION**

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# The Soil Solution

## The Nutrient Medium for Plant Growth

By

FRANK K. CAMERON

In Charge, Physical and Chemical Investigations, Bureau of Soils,  
U. S. Department of Agriculture

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## Preface.

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It has long been the custom to regard soil chemistry from one of two diametrically opposed points of view. Either, it has been considered extremely simple, or complex and hopelessly difficult. In either case the impression has generally prevailed that practical work in soil chemistry consists in treating the soil with some solvent or other and analyzing the resulting solution for "available" plant food elements; in other words, that the chemist's role in soil studies is merely that of an analyst.

Soil chemistry is complex, but not by any means hopelessly so. Unfortunately, the complexity of most of the problems presented has deterred the student of pure chemistry from attacking them, and because they do not offer any material pecuniary rewards, they have not appealed strongly to the investigator in applied chemistry. Investigations in soil chemistry, for their own sake, or for the sole purpose of increasing the sum total of human knowledge concerning the phenomena taking place in the soil, have been comparatively rare. The subject has generally been regarded from the analytical point of view and as incidental to agronomic studies.

One purpose of this little book is to show the investigator in chemistry who is not limited by the condition that his work must bring some personal financial return, that the soil and its problems offer a field for his efforts quite worthy of ranking alongside the most interesting branches of pure chemistry, as well as being of the very highest importance to the development of the welfare of the human race. Another purpose is to point out the line of attack upon the problems of soil chemistry which at this time offers the largest opportunity for results. In how far the details of the story in the following pages are correct, time with its further investigations will tell. In a sense, the correctness of the details is of secondary importance. It is of the first importance, however, that there should be a general recognition that soil phenomena are essentially dynamic in character, and that the investigation of the properties of the soil solution and its relation to crop production is a procedure certain to yield results of positive value.

Again, it is a purpose of this book to make available to students of agriculture, a systematic outline of the work so far accomplished in this particular field. It is to the students of to-day from whom are to come the investigations of the near future that the book is particularly addressed. Some of the details presented in the following pages are matters on which opposed opinions are now held strongly by different authorities, and to the unbiased minds of the coming investigators must be left the decision as to how closely the truth has been approximated in what is written to-day. The field of effort covered by this book is one in which there is an increasing activity, and new facts and deductions will inevitably bring modifications to present opinions. To encourage this further acquisition of knowledge is the main purpose of the book.

The material brought together in this book has been presented to the faculties and students of several of our Agricultural Colleges, in the form of a short course of lectures. In large part, moreover, it has been published in Volume XIV of the Journal of Physical Chemistry. To make it accessible to and more easily read by one familiar with the progress of technical soil investigations, it has been recast in its present form.

It has been assumed that the reader will have a fair working knowledge of the concepts of modern chemistry. Nevertheless, an effort has been made to avoid technical terms so far as this can be done without undue sacrifice of lucidity of expression. Free references have been made to the bulletins of the Bureau of Soils, U. S. Department of Agriculture, because they are generally accessible to the American student, and because in them will be found detailed discussions and bibliographical material pertinent to the subjects outlined here. To his coworkers, the author is indebted for many criticisms and suggestions; and more especially in the making of the book is he indebted to Mr. S. C. Stuntz.

Washington, D. C.

1911.

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# **AN INTRODUCTION TO THE STUDY OF THE SOIL SOLUTION.**

## **Chapter I.**

### **THE SOIL.**

The soil, or that part of the land surface of the earth adapted to the growth and support of crops, is a heterogeneous mixture composed of solids, gases and a liquid, and containing living organisms. There are present: mineral debris from rock degradation and decomposition; organic matter from the degradation and decomposition of former plant and animal tissues; the soil atmosphere, always richer in carbon dioxide and water vapor and possibly other gases than the atmosphere above the soil; living organisms, such as various kinds of bacteria and fungi, with the products of their activities, notably the "nitrogen carriers" and the enzymes; and finally the soil moisture, a solution of products yielded by the above components and in equilibrium or approaching equilibrium with the solids and gases with which it is in contact.

In its relation to crop plants,<sup>1</sup> that part of the soil of immediate importance is the soil moisture. From this solution the plants, through their roots, draw all the material involved in their growth, except the carbon dioxide absorbed through their leaves. The soil solution is the natural nutrient medium from which the plants absorb the mineral constituents which have been shown to be absolutely essential to their continued existence and development. And from this solution plants sometimes absorb dissolved organic substances, but such absorptions are probably adventitious and incidental to the growth of the plant in a particular environment. While it appears certain

<sup>1</sup> By crop plants are meant the ordinary green plants employed in agriculture. As is well-known, the fungi as well as certain parasitic and saprophytic non-green seed plants obtain their nutriment in a very different way from ordinary green crop plants.

that no organic substance in the nutrient medium is necessary to the maintenance of plant growth, nevertheless organic substances are probably always present under natural conditions. They may or may not be absorbed by the plant and may affect it beneficially or otherwise.

The study of the soil solution is of the first importance in the investigation of the relation of the soil to plant growth, and in the following pages there is given an outline of our present knowledge of the chemical principles involved, with such discussion of the physical and biological factors as is essential to an orderly presentation of the subject.

To understand clearly the relations of the soil solution to the soil as a whole and to the plant which it nourishes, it is desirable to consider some attributes of soils in general. Every soil, no matter of what type it may be, is a complex system. In it various processes are continually in operation, excepting possibly in the extreme case when it remains frozen for a time at some definite temperature. The resultant or summation of these processes, whether expressed in plant production or otherwise, will vary from time to time, both quantitatively and in direction; for instance, as to the amount and kinds of plant growth it produces. That is to say, any particular soil area is seemingly an organic entity, functioning according to its own inherent properties, but subject to the modifying influences of environment, as by exceptional climatic extremes, flood, fire, and especially by artificially imposed agencies of control.

From the practical point of view the problem of the soil in its relation to crop production is like the problem of the factory or of any other industrial endeavor, in that it is a problem of management or control. The soil possesses this distinction, however, that it is both the raw material and the factory.<sup>1</sup> The processes involved are physical, chemical and

<sup>1</sup> According to S. W. Johnson—Some points of agricultural science, Am. Jour. Sci. (2), 28, 71-85 (1859)—“The soil (speaking in the widest sense) is then not only the ultimate exhaustless source of mineral (fixed) food, to vegetation, but it is the storehouse and conservatory of this food, protecting its own resources from waste and from too rapid use, and converting the highly soluble matters of animal exuviae as well as of artificial refuse (manures) into permanent supplies.”

biological, are always numerous and interdependent, and are never (speaking generally) exactly the same, so that each soil possesses marked individuality. No matter how soils may be classified, as for instance into provinces, series and types,<sup>1</sup> the fact remains that the soil of the individual field has properties which give it a crop-producing power, an adaptation to a specific crop or crop rotation, or a responsiveness to cultural treatment, which can not be anticipated in any other field. Consequently, there is no possibility of reducing soil management or agriculture to the state of an exact science. That is to say, scientific investigation of the problems involved cannot be expected to yield absolute results, although furnishing the best possible basis on which to form judgments. Soil management, like other agricultural practices, is an art, more or less well founded on scientific principles, perhaps, but susceptible of much higher development as the scientific principles involved become better understood.

<sup>1</sup>For definitions, see Soil Survey Field Book, 1906, Bureau of Soils, U. S. Dept. of Agriculture, pp. 15-24. On the ground that experience has shown that genetic classifications are the ones which have generally persisted and proved the most useful, objection might be made to the classification just cited. But a careful inspection of the results of the Soil Survey by the U. S. Department of Agriculture will show that while not categorically stating the fact, to all intents and purposes it has employed a genetic classification. This is exemplified by the fact that its delineation of soil provinces corresponds quite closely with the recognized physiographic provinces of the United States. See map accompanying *Soils of the United States*, by Milton Whitney, Bull. No. 55, Bureau of Soils, U. S. Dept. Agriculture, 1909.

## **Chapter II.**

### **SOIL MANAGEMENT OR CONTROL.**

Aside from such devices as greenhouses, wind-breaks, etc., which have a local application only, there are three general methods of soil control: tillage methods, such as plowing and harrowing; rotation of crops; and the use of soil amendments or "fertilizers."

The existing knowledge regarding tillage methods is generally considered to be fairly satisfactory. The purposes are well understood, namely, to break up and "fine" the soil,<sup>1</sup> to keep down weeds, and by forming mulches to decrease the loss of water by evaporation. Not much increase is being made in our theoretical knowledge of this subject, although mechanical improvements in the implements of tillage are being and will undoubtedly continue to be made.

The existing knowledge concerning crop rotations is fairly extensive, but it is almost entirely empirical. Some at least of the purposes served by a rotation of crops are fairly well known, such as the elimination of weeds or lower types of parasitic growth associated with particular crops; the introduction of humus by a grass crop or a green manure crop, especially by the *Leguminosae* with their symbiotic *Azobacteria*; the improvement in the structure or arrangement of the soil particles by alternating deep-rooted and shallow-rooted crops; the avoidance of continually growing a crop in the presence of its own excreta, products of decay, etc.; and lastly, economic and market considerations.

The existing knowledge of fertilizers, in spite of a vast amount of work and an enormous literature, is still very meagre and it also is almost entirely empirical; and this because studies on the subject have been dominated for three-quarters of a century by one theory almost to the exclusion of any other. The exponents of this theory have generally assumed that the action

<sup>1</sup> Actually, to granulate the soil. "Fine" would seem to be a misnomer, but its agricultural significance is well understood, and it has the sanction of long usage in the literature.

of fertilizers is on the plant rather than on the soil, and is independent of other factors. That is, while it is admitted that other factors influence plant growth, it has been held that the effect of the fertilizer is not to modify the influence of the other factors but to directly influence the plant by increasing its food supply. As a consequence, it has also been generally assumed that the influence of fertilizers is additive, that is, the increase in yield of crop is proportional to the increase in fertilizer added, and the increase in yield produced by adding two fertilizers is the sum of the increases which would have been produced by each alone. In this form the theory is essentially a quantitative one, and fertilizer practice should be easily susceptible of control by chemical analyses. But the large mass of data obtained from plot experiments shows that fertilizer effects are not additive. Indeed, the addition of some one or more fertilizer constituent is sometimes followed by a decreased yield. For example, about 20 per cent. of the trials of fertilizers on soils growing corn and reported by the American State Experiment Stations show a decreased yield. And furthermore, in spite of the quantitative character of the theory, and the numerous analyses of soils and of plants which have been made, there is yet lacking any authoritative method for determining in quantitative terms the fertilizer needs of a soil. That analytical methods have a very restricted value in indicating even qualitatively the fertilizer needs of the soil is evidenced by the fact that within the past few years a number of the State Experiment Stations have publicly announced their unwillingness to undertake them.<sup>1</sup>

<sup>1</sup> In this connection see: The texture of the soil, by L. H. Bailey, Cornell University Agr. Expt. Sta., Bull. No. 119, (1896); Suggestions regarding the examination of lands, by E. W. Hilgard, University of California, College of Agriculture, Circ. No. 25, (1906); Chemical analysis of soils, by William P. Brooks, Massachusetts Agr. Expt. Sta. Circ. No. 11, (1907); Testing soils for fertilizer needs, by F. W. Taylor, New Hampshire Agr. Expt. Sta., Circ. No. 2, (1908); The uses and limitations of soil analysis, by J. T. Willard, The Industrialist, Kansas State Agricultural College, 34, 291, (1908); Soil analysis, by Wm. Frear, Pennsylvania Agr. Expt. Sta., Chem. Circ. No. 1; How to determine the fertilizer requirements of Ohio soils, by Chas. E. Thorne, Ohio Agr. Expt. Sta., Circ. No. 79, (1908); Concerning work which the station can and cannot undertake for residents of the state, by Joseph L. Hills, Vermont Agr. Expt. Sta., Circ. No. 3, (1909).

The common procedure has been to define some arbitrary percentage limit in the soil, below which the soil is supposed to require fertilizers. But the amount of fertilizer to be applied is suggested on the indefinite basis of "experience." Thus, Hilgard, in an interesting discussion of this subject,<sup>1</sup> quotes Dyer as showing that "on Rothamsted soils of known productiveness or manurial condition, it appears that when the citric acid extraction yields as much as 0.005 per cent. of potash and 0.010 per cent. of phosphoric acid, the supply is adequate for normal crop production, so that the use of the above substances as fertilizers would be, if not ineffective, at least not a profitable investment." Hilgard himself sets limits as determined by strong hydrochloric acid digestion; thus a soil containing upwards of 0.45 per cent. ( $K_2O$ ) does not need this substance as a fertilizer, while one containing below 0.25 per cent. does need it at once, and intermediate percentages indicate that potash fertilizers would probably be profitable; the corresponding upper and lower limits for phosphoric acid are set at 0.10 per cent. and 0.05 per cent. But Hilgard points out that various things, such as the content of lime, or the texture of the soil, may materially alter these limits. In a very interesting set of experiments in which white mustard was grown in various soils, and these same soils diluted with various amounts of dune sand which had previously been extracted with strong hydrochloric acid, he found that the plants did best when the soils had been diluted with four times their weight of the extracted sand. This was the case even with a pulverulent sandy loam; and with a black adobe, the best results were obtained when the diluted soil contained but 0.15 per cent. potash ( $K_2O$ ) and 0.04 per cent. phosphoric acid ( $P_2O_5$ ). It also appears that Hilgard regards soil analyses of value only in the case of virgin soils or soils which have been out of cultivation, and in common with other authorities, he fails to point out how to determine the *amount* of fertilizer needed by lands.

It is clear, therefore, that the principles underlying the practice or art of soil management and crop rotation are in a state of

<sup>1</sup> Soils by E. W. Hilgard, 1906, p. 339, *et seq.*

development far from satisfactory, and scientific methods of soil control yet wanting.<sup>4</sup> Recent activities in soil investigations, however, justify the hope that much improvement is to be anticipated, and the application of the modern methods of physical, chemical, and biological research to the soil problem promises a sure and probably rapid advance in this branch of applied science.

<sup>4</sup> It should, of course, be borne in mind that soil factors are not the only ones in crop production. Control by seed selection, breeding of standard types of plants, etc., may be, and probably is, more highly developed than control by soil factors. The same might possibly be claimed for moisture supply in irrigated areas; but on the other hand, such factors as the bacterial and lower life processes in the soil are generally under little or no control, and as a rule the amount and distribution of sunlight under none at all. A notable effort has been made in the last case with shade grown tobacco (see Bulletins Nos. 20 and 30, Bureau of Soils, U. S. Dept. of Agriculture) and a few cases are known where shade crops are employed, but not in general agriculture.

## Chapter III.

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### SOIL ANALYSIS AND THE HISTORICAL METHODS OF SOIL INVESTIGATION.

Owing to the labors of Davy, Boussingault, de Saussure, Liebig, Sachs, Knop, Salm-Horstmar, and other scarcely less distinguished savants, it has been clearly shown that *growing plants need certain mineral elements in order to maintain their metabolic functions*, and that *these mineral elements can be obtained, under normal conditions, from the soil*. All subsequent investigation has confirmed these statements and they can now be accepted as facts with as much assurance as any known law of nature.

The determination and formulation of these two fundamental facts came at a time when analytical chemistry was being rapidly developed and was finding wide and useful applications in numerous fields of activity. It was natural, therefore, that analytical chemistry should be enlisted in this new field of work, obviously of the first importance to the welfare of mankind. It was early found, however, that the chemical analysis of a soil fails to explain its relative productivity. In other words the content of a soil with respect to potash, phosphoric acid, or other mineral plant-food constituent, bears no necessary relation to its crop-producing power. Many cases were found where one soil "analyzed well" but did not produce as large a crop as another soil which "analyzed poor."<sup>1</sup> To meet this difficulty a subsidiary hypothesis was brought forward, which rapidly gained general acceptance although lacking experimental support.

This hypothesis supposes that the mineral constituents of the soil are present in two different chemical conditions or distinct kinds of combinations, one of which readily gives up its constituents to growing plants, while the other does not; and the constituents have, therefore, been called respectively "available"

<sup>1</sup> See also, Die Aufnahme der Nährstoffe aus dem Boden durch die Pflanzen, von J. König und E. Haselhoff, Landw. Jahrb., 23, 1009, 1030, (1894).

and "non-available." It would appear from his writings that Liebig regarded this distinction as applying to the "absorbed" or "adsorbed" mineral matter; that is, on the one hand the material held in or upon the soil grains by surface forces, and on the other the chemically combined constituents in the minerals themselves. We know that Liebig was much impressed by the absorption experiments of Way, and himself did much work in this field.<sup>1</sup> But the great body of soil investigators has evidently held to the opinion that there are two general classes of minerals in the soil. Some have held that the "available" potassium is held in zeolites or "zeolitic" minerals, an interesting example often cited being glauconite or "green sand marl," which sometimes contains phosphorus as well as potassium;<sup>2</sup> in minerals which are easily broken down by alkaline solutions, as by sodium carbonate solutions or ammonia; or in minerals which are easily broken down by organic acids supposedly excreted from the roots of growing plants, or formed by the decay of plant tissue.<sup>3</sup>

With the advent of this idea of a distinction between the available and non-available mineral plant-food elements in the soil, came attempts to distinguish them by analytical methods. Of these attempts we now have a bewildering array, most of

<sup>1</sup> Way was misled, as we now know, in considering the results of his absorption experiments with soils as merely metathetical reactions; see Absorption by soils, by Harrison E. Patten and William H. Wagaman, Bull. No. 52, Bureau of Soils, U. S. Dept. Agriculture, 1908.

<sup>2</sup> The formation of zeolites in the soil has often been assumed, but has not yet been proven; see Rocks, rock weathering and soils, by George P. Merrill, 1909, p. 363.

<sup>3</sup> The classic experiments of Sachs, in producing etchings on marble slabs, and the etchings observed occasionally on rock surfaces are the proofs universally cited. The experiments of Czapek, who substituted slabs of aluminum phosphate and other substances for the marble, and those of Kossowitch, show that the action can be accounted for more satisfactorily and reasonably as due to dissolved carbon dioxide. In fact such etchings can be produced on marble slabs by laying platinum wires upon them and covering with moist soil, or cotton, or mats of filter-paper; see Bull. No. 22, p. 14, and Bull. No. 39, p. 41, Bureau of Soils, U. S. Dept. Agriculture.

them frankly empirical. For instance, Hilgard, in his classical investigation of the cotton soils for the Tenth Census, treated his soil samples with an excess of hydrochloric acid, evaporated to dryness, extracted with water, and regarded the extracted mineral constituents as available. In Germany, a method similar to Hilgard's is now in common use, while in France nitric acid is preferred generally because it is supposed to have peculiar solvent powers on soil phosphates. In the United States the "official method" of the Association of Official Agricultural Chemists is to keep to grams of the soil in contact with 100 cc. of a solution of hydrochloric acid (specific gravity 1.115) at the boiling point of water for exactly 10 hours. In England the popular method is that proposed by Dyer, namely, to treat the soil with a 1 per cent. citric acid solution, this strength of solution being supposed at one time to represent the average acidity of root sap. Maxwell, in Hawaii, and afterwards in Australia, claimed good results for the extraction of the soil with a 1 per cent. solution of aspartic acid, this acid being employed on the erroneous ground that the organic acids of the soil are amido acids, and that these are the effective agents in dissolving the soil minerals and rendering their constituents "available." The Kentucky Agricultural Experiment Station favors an N/5 nitric acid solution,<sup>1</sup> but does not recommend its use for soils of other localities, while in a contiguous state, the Tennessee Station favors the "official" method.<sup>2</sup> Many other methods have been proposed, but the foregoing are typical and sufficient to illustrate the present status of soil analysis.

It is clear that these several methods must give differing results. And it is not clear that any one of them is to be preferred to the others for any reasons than analytical convenience. There is no reason to expect that the proportion of solvent to soil required in these methods bears any relation whatever to the mechanism of absorption by plant roots. And the attempts

<sup>1</sup> Soils, by A. M. Peter and S. D. Averitt, Bull. No. 126, p. 66, (1906).

<sup>2</sup> The soils of Tennessee, by Charles A. Mooers, Bull. No. 78, p. 49, (1906).

to simulate the properties of plant sap in some of these solvents are obviously illogical, for the plant sap does not come in contact with the soil grains, except through an accidental destruction of the plant.

Naturally, comparisons were attempted between the amounts of the mineral constituents extracted from a soil by these various solvents and the amounts taken up by crops growing on the soil. It was found, however, that the amount of any given mineral constituent extracted from the soil by a solvent is not, generally, the same as that taken up by the plant. Moreover, the ratio of one constituent to another in the extract bears no definite relation to the ratio of these constituents in the plant. Nevertheless many efforts were made to establish "factors." For instance, the percentage of potash extracted from the soil of a field by hydrochloric acid is some multiple of the percentage removed by a wheat crop; it was sought to determine this multiple, assuming it to be a definite ratio and a natural constant, and it was designated as the potash factor. But there is a different factor for phosphorus, another for calcium, and still others for each and every constituent. The factors found for a soil from one area generally do not hold for a soil from another area. Again, different factors obviously must be used for different crops. And, finally, the whole scheme becomes hopeless when it is realized that the same crop will yield widely varying ash analyses, depending upon the cultural methods employed, the judicious selection of seed, the amount and distribution of rainfall and sunlight, and possibly other agencies, all of which affect the growth and absorptive functions of the plant to as great an extent as does the particular soil upon which it may be growing.

Moreover, from the purely analytical point of view the situation is no better. For instance, the addition of potassium in the amounts usually employed in ordinary fertilizer practice generally does produce a noticeable effect on the yield of crop. The average application of potash ( $K_2O$ ) is certainly less than 50 lbs. to the acre. It is customary to consider the surface foot of soil as the region affected by the fertilizer, and an acre foot

*in good moisture condition weighs about 4,000,000 lbs.* To be conservative, let it be assumed that 60 lbs. of potash have been added to 3,000,000 lbs. of soil. The official method of the Association of Official Agricultural Chemists calls for the determination of the potash in 2 grams of soil, which on the basis of the present assumption calls for the estimation of an added amount of 0.00004 gram of potash or 0.002 per cent. Taking as an example the report of the Association of Official Agricultural Chemists for 1895<sup>1</sup> there are given the following results obtained independently by a number of analysts, on soils which had presumably been sampled by the referee with all possible care:

POTASH CALCULATED AS PER CENT. OF THE FINE DRIED EARTH.

Analyst	1		2		3		4	
	Per cent.	Var.						
A .....	0.359	0.044	0.154	-0.002	..	..	..	..
B .....	0.345	0.030	0.112	0.044	0.380	0.051	0.104	-0.050
C .....	0.354	0.039	0.235	0.079	0.396	0.067	0.225	0.071
D .....	0.260	0.055	..	..	..	..	..	..
E .....	0.373	0.058	0.179	0.023	0.365	0.036	0.175	0.021
F .....	0.210	-0.105	0.130	-0.026	0.220	-0.109	0.109	-0.045
G .....	0.304	-0.011	0.125	-0.031	0.286	-0.043	0.158	0.004
Mean .....	0.315	..	0.156	..	0.329	..	0.154	..

Not only do the individual determinations show differences far in excess of 0.002 per cent., but the differences between each individual reading and the mean is greater than 0.002 per cent., so that it is evident from these results that the analytical procedure fails to recognize appreciable amounts of the so-called available plant foods. Consequently the "acid digestion" of a soil fails of the purpose for which it was designed, and it is one of the mysteries of chemical history that so much time and energy have been devoted to such a hopeless quest.

This state of affairs is the more surprising when the lim-

<sup>1</sup> Proceedings of the Twelfth Annual Convention of the Association of Official Agricultural Chemists, Bull. No. 47, Division of Chemistry, U. S. Dept. Agriculture, p. 36, (1896).

iations of the analytical procedure are considered. The data tabulated above indicate that the analyses were made with an exactness that justifies a statement to three decimal places, that is, to three significant figures; and in fact, as was shown, such is necessary if the figures are to have any significance regarding fertilizer applications. It is obvious that the analysis of a finely pulverized definite mineral or rock is less subject to error than a sample of soil sifted through a 2 mm. mesh. Yet the U. S. Geological Survey commonly reports its analytical data to only hundredths of a per cent., that is, to two decimal places. What variation may be expected in duplicate determinations by the same analysts it is difficult to say, for such duplicates are not commonly published.<sup>1</sup> In spite of the widespread view that the chemical analysis of a soil is a statement of great accuracy, it is improbable that as usually determined the potash content is correct to three or even two significant figures; it is also doubtful if the phosphoric acid content is correct to even one significant figure, if the total amount is below 0.1 per cent. of the soil. That these determinations have a higher accuracy than here stated is not shown by an inspection of the literature including the fairly numerous results reported in the annual Proceedings of the Association of Official Agricultural Chemists.

It was early felt by some investigators that soil analyses were unsatisfactory for studying the relation of the soil to the food requirements of a crop, and a second method was devised, namely, the growing of a crop, and determining the amount of mineral constituents removed from the soil by analyzing the ash of the crop. From the point of view of practical soil management this procedure involves the serious difficulty of being first obliged to get the crop before determining what must be done to best get it. It apparently has the scientific advantage of direct-

<sup>1</sup> See: On the interpretation of mineral analyses, by S. L. Penfield, Amer. Jour. Sci., (4), 10, 33, (1900); The analysis of silicate and carbonate rocks, by W. F. Hillebrand, Bull. No. 305, U. S. Geol. Surv., 1907; Manual of the chemical analysis of rocks, by H. S. Washington, 1904, p. 24; Ueber Genauigkeit von Gesteinanalysen, von M. Dittrich, Neues Lehrbuch für Mineralogie und Palaeontologie, 2, 69, (1903).

ness in determining the mineral needs of the plant from the plant itself. If these needs were constant, the advantage would be real, but as already mentioned, one and the same plant may have a very different ash content as the result of different cultural methods, different climatic and seasonal factors, as well as different soils. Generally, a poor crop has a higher percentage of ash content than a good crop, and sometimes the poor crop may remove from the soil more in absolute amounts of some one or other of the ash constituents than does the good crop. The ratio of the ash constituents is by no means constant for any one crop, and of course varies with different crops.<sup>1</sup> Finally, it is now known that the amount of the several mineral nutrients which a soil must furnish to a crop in the earlier stages of growth is greater than the crop contents at maturity,<sup>2</sup> consequently an analysis of the ripe crop would not indicate the plant's drain upon the soil at all growing periods. So that, while ash analyses have taught some important things concerning plant growth, they have of necessity failed as guides or criteria of the crop-producing power of a soil, its fertilizer requirements, or its content of "available" plant-food.

A third method of soil investigation, also essentially analytical in character, is the plot or pot test. The difference between a plot or pot experiment is mainly one of size, although it is claimed, and with a certain amount of justice, that the plot experiment more nearly approximates actual practice, and should be given a somewhat different consideration than the more readily controlled pot experiment. Here again it has to be considered that seasonal factors and factors other than the soil play a relatively large part in the production of the crop, so that conclusions regarding the productivity of a soil can not be

<sup>1</sup> For a brief but comprehensive discussion of ash analyses see, The ash constituents of plants, etc., by B. Tollens, Expt. Sta. Rec., 13, 207-220, 305-317, (1901-02).

<sup>2</sup> Über die Nährstoffaufnahme der Pflanzen in verschiedenen Zeiten ihres Wachstums, von Wilfarth, Römer und Wimmer, Landw. Vers.-Sta., 63, 1-70, (1905); Plant food removed from growing plants by rain or dew, by J. A. Le Clerc and J. F. Breazeale, Year Book, U. S. Dept Agriculture, 1908, p. 389-402.

drawn from one season's crop. Also, nowadays it is recognized generally that continuous growing of one crop is an incorrect practice, and a rotation should be followed and repeated several times before conclusions regarding the productivity of the soil are justified. If, however, the rotation has been well managed, the cultivation, fertilizing and soil management generally been well done for sixteen, twenty or more years, the soil has materially changed, and there can be no assurance that the treatment then best for it, is that which was best at the beginning of the experiment. Therefore the method throws no certain light on the productive power of the soil, or the availability of its mineral plant-food constituents. Although much has been learned from plot experiments, and especially from the better controlled pot experiments, they are inadequate to meet the fundamental problem of the relation of the chemical characteristics of the soil to its crop-producing powers.

## **Chapter IV.**

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### ***THE PLANT-FOOD THEORY OF FERTILIZERS.***

The guiding principle in soil investigations for about three-quarters of a century and until the past few years has been the assumption that the principal function of the soil is to furnish mineral nutrients to the plant, and that, to supply a lack in the soil, fertilizers are added because of the mineral plant nutrients they contain. This theory has apparently much to support it; actually, however, the evidence usually cited accords better with a more comprehensive generalization which will be formulated in a later chapter. It is attractively simple. It will be shown later, however, that this very simplicity is an argument against its validity.

Those substances which experience has shown to be useful soil amendments usually contain one or more of the constituents necessary to plant metabolism, commonly phosphorus, potassium, nitrogen or calcium. Fertilizers do not always produce increased yields of crops, but it has been usual to consider bad results as due to other more or less extraneous causes. Moreover, as will appear later, crop yield is as strongly affected by some substances containing no mineral plant nutrient as by ordinary fertilizers. Again, the plant-food theory has been apparently confirmed by the popular misconception that crop yields are decreasing. Government statistics, however, indicate very positively that crop yields are increasing in Europe as well as in America, more in areas where the acreage is stationary than in areas where the acreage is increasing, and in areas where fertilizers are not used as well as in areas where they are used. Analyses of European soils which have been cropped for centuries show no characteristic differences from the newer soils of the United States.<sup>1</sup> It is true that, from bad management or other causes, individual fields where crop production has fallen

<sup>1</sup> A study of crop yields and soil composition in relation to soil productivity, by Milton Whitney, Bull. No. 57, Bureau of Soils, U. S. Dept. Agriculture, 1909.

off are not uncommon. But that such a condition is general or that it can be associated generally with a decreased content in the soil of any particular mineral substance or substances, is a conclusion not sustained by the available data.

The plant-food theory of fertilizers must now be regarded as entirely insufficient. Granting that it has been useful in the past and has occasioned much valuable work, it seems to have reached the point which another simple and temporarily useful theory, the phlogiston theory of combustion, reached shortly before the plant-food theory of fertilizers was evolved. Just as the phlogiston theory passed away when the elementary nature of oxygen was established and Lavoisier taught the scientific world to use the balance, so the plant-food theory of fertilizers must pass with increasing knowledge of the relation of soil to plant and the application of modern methods of research to the problem.

## Chapter V.

### THE DYNAMIC NATURE OF SOIL PHENOMENA.

In soil investigations, until recently, the assumption has been made, more or less explicitly, that any given soil mass, as for instance a field, remains fixed or in place indefinitely. It has been admitted, of course, that some physical, chemical and biological processes might be taking place in the soil, but these have been regarded as relatively unimportant in their effects upon the soil mass *in toto*. It has been assumed that the only important change taking place in the soil is a loss of mineral plant nutrients, partly by leaching, partly by removal in the garnered crops. In other words, the soil has been regarded as a static system. This is a fundamental error. In studying the soil as a medium for crop production, we must consider the plant itself, or at least that part of the plant which enters the soil, namely, the root; the solid particles of the soil; the soil water, or the aqueous solution from which the plant draws all the materials for its sustenance, excepting the carbon dioxide absorbed by its aerial portions; the soil atmosphere; the biological processes taking place. The one common characteristic of all these things is that they are continually in a state of change; therefore the soil problem is essentially dynamic.

The root of a growing plant is always moving.<sup>1</sup> The amount of motion may be small or large, depending upon the surround-

<sup>1</sup> In order to penetrate the soil, a living root must be capable of exerting large pressures, and indeed, the magnitude of these pressures has been determined for some cases. See, for citations of the literature Pfeffer, Plant Physiology, translated by Ewart, 1903, Vol. 2, p. 124 *et seq*. But it can not be doubted that, in general, root movement is much facilitated and perhaps directed by movements among the soil particles. As the absorbing tip of the root removes film water from the adjacent soil grains, there is a necessary rearrangement of these grains with a shrinking away from the tip, which then moves forward by taking advantage of the movements among the soil grains.

ing conditions or attendant circumstances, but cessation of motion means the death of the root. This becomes evident from a consideration of the mechanism of root growth. The living root absorbs and excretes water and dissolved substances through a restricted area just back of the root tip or the tips of the root hairs. While absorption is taking place, however, there is a deposition of denser material over the absorbing area, or "root corking." But coincident with the corking process, the tip is pushed forward between the soil grains into the nutrient medium, new cells are formed and a new absorbing surface continually brought into functional activity. A failure of the plant root to move forward in this way would mean a reabsorption of root effluvia with harmful consequences to the plant, or a corking over of the root without further formation of absorbing surface and with consequent cessation of its functioning. This would mean the inevitable death of the root, and, if general, of the whole plant. It is clear, therefore, that root penetration and absorption of plant nutrients are essentially dynamic.

The solid components of the soil are always in motion. Every soil, no matter how flat the area or how well protected by vegetal covering, suffers some translocation of soil material through rains, as is evidenced by suspended material in the run-off waters. On hillsides this is shown by the soil accumulating on the "up" sides of fences, especially stone fences. In the aggregate this movement is probably quite large everywhere. It is manifestly so in the watersheds of many of the world's important rivers as shown by their muddy waters and the formation of deltas, sometimes of great area and agricultural importance.

With the saturation or approach to saturation of the surface soil the particles are more easily moved among themselves by an extraneous force. It is very rarely that the surface of a field is a dead level. Consequently when the soil is wetted, the gravitational force on the individual soil grains produces a more or less pronounced "creeping" effect down hill. On decided

slopes this soil creep is believed to be of great importance in connection with soil erosion.<sup>1</sup>

As important as is the translocation of material by water, quite as important probably is that produced by the winds. These are blowing all the time, uphill as well as down, and their range of action is thus far wider than is that of rain and flood. The effectiveness of the wind as a translocating agency is seldom realized or even suspected by the layman, although it is commonly known that the air always contains some dust, and dust storms are familiar phenomena. That soil material can be carried long distances is certain, however, as for instance the sirocco dust, often carried from the Sahara over Europe.<sup>2</sup> Dust carried high into the air by volcanic eruptions sometimes travels enormous distances, as in the case of the eruption of Krakatoa, when such material is reported to have traveled thousands of miles, and volcanic debris from the eruptions at Soufrière fell upon ships several hundred miles distant. Arctic explorers have reported the finding of wind-borne soil materials over the polar ice, and mountaineers have observed similar

<sup>1</sup> Soil erosion is undoubtedly one of the greatest economic problems of the time, and yet there is scarcely any subject about which there are current so many popular misconceptions. In the rivers and to those who use the rivers the water-borne soil material is an unmitigated nuisance, save possibly to a few cultivators of low-lying lands who for one reason or another, may flood their fields for the sake of the silt deposited. To the upland farmer, however, erosion is not only a necessity of natural conditions which can not be avoided entirely, but under proper control it may be even a blessing. The scalped and gullied hillsides, a trial and unnecessary disgrace to the owner, are probably not the main sources of the material which finds its way to the river. On the contrary, what are regarded usually as well-tilled fields supply the greater part of the suspended material in the rivers. The problem of erosion on the farm is not merely to check gullying and scalding, and deepening of stream heads, but to so adjust both cropping system and cultural methods as to secure a reasonable translocation of surface soil material with a minimum contamination of the neighborhood streams. See, *Man and the earth*, by Nathaniel Southgate Shaler, 1905.

<sup>2</sup> For a comprehensive discussion of wind as a translocating agent, see: *The movement of soil material by the wind*, by E. E. Free, Bureau of Soils, Bull. No. 68, U. S. Dept. Agriculture.

deposits on snow-capped peaks. Soil material on roofs and similar inaccessible places has been observed many times, and testifies to the continual activity of the wind. The burial of objects even of considerable size by wind-borne soil gives like testimony.

Measurements of the amount of action of wind in translocating soil material are rare and probably have a qualitative value only. But Udden<sup>1</sup> in what appears to be a conservative calculation, finds "the capacity of the atmosphere [over the Mississippi Valley] to transport dust is 1000 times as great as that of the [Mississippi] River." The wind seldom is carrying anything like so great a load as it is capable of carrying. That is, the wind in its attack upon the land surface does not ordinarily obtain so large an amount of material capable of being wind-borne as it is possible for the wind to carry when suitable material is artificially provided. It should be remembered that, speaking generally, the velocity of the wind is lower just at the surface of the ground than at heights above, and it is necessary to get the soil material above the surface before the wind can exercise its full efficiency as a carrying agent.

Moreover, wind-borne material is constantly being deposited as well as being removed from the land surface. It is evident, however, that this movement of soil material by winds is very great, and there is no reason to believe that it is of any less importance in other areas than in the Mississippi Valley. It is also evident that the individual grains in any surface soil of any particular field or area are continually and more or less rapidly changing, and the farmer is not dealing to-day with just the same soil complex he faced a few years back, or will face a few years hence.

But besides the movements of the solid components of the soil by translocating agencies, other movements are constantly taking place. Whenever a moderately dry soil becomes wetted, it "swells up" until a certain critical amount of moisture is present above which there is a shrinking. But as a wet soil

<sup>1</sup> Erosion, transportation and sedimentation performed by the atmosphere, by J. A. Udden, *Jour. Geol.*, 2, 318-331 (1894).

dries out again below the critical amount, there is again a shrinking. As it is always either raining or not raining, soils are always either getting wetted or are drying. Consequently the individual grains are continually moving about among themselves. A heavy object, such as stone, when left on the ground gradually sinks into it.<sup>1</sup> Earthworms, burrowing animals and insects are continually at work in most arable soils. The action of frost in "heaving" a soil is familiar to everyone. Not so well known, however, is the fact that the apparently superficial cracks which occur to a greater or less extent in every soil, under drought conditions, are in reality quite deep, extending well into the subsoil. By the edges breaking off, and by wind- and water-borne material being carried in, considerable surface soil is thus brought into the subsoil. Through these various agencies, therefore, the solid components of the soil are continually subject to much mixing; subsoil is becoming surface soil, and to some extent *vice versa*. An important result of these various processes is the bringing into the surface soil of degradation and decomposition products from underlying rocks. The processes involved are essentially dynamic.<sup>2</sup>

The soil solution is also a dynamic problem. When the rain falls on the soil, a part, the "run-off," flows over the surface and finds its way into the regional drainage; a part immediately evaporates into the air, and is designated as the "fly-off;" a third part, the "cut-off," enters the soil.<sup>3</sup> The cut-off water penetrates the soil by way of the larger openings and interstices,

<sup>1</sup> On the small vertical movements of a stone laid on the surface of the ground, by Horace Darwin, Proceedings of the Royal Society of London, **68**, 253-261, (1901). On the other hand, geological literature would probably furnish numerous references to the heaving out of boulders, probably as the result of successive freezings and thawings of the soil. The shape of the stone as well as the specific nature of the movements of the soil particles evidently has an important influence in determining whether the stone sinks into the soil or *vice versa*.

<sup>2</sup> It is clear that as the soil is continually changing through physical agencies, the chemical analysis of it can not be expected to furnish evidence as to the mineral constituents removed by crops or by leaching.

<sup>3</sup> This terminology has been suggested by Dr. W. J. McGee.

and mainly under the influence of gravity. For convenience this downward-moving water is designated as "gravitational" water. It moves through the soil with comparative rapidity and a portion reappears elsewhere as seepage water, springs, etc. But with the return of fair-weather conditions at the surface, there is increased evaporation and augmentation of the fly-off, and there is developed a drag or "capillary pull" on the water below. A large portion of the cut-off thus returns to the surface, mainly through films over the surface of the soil grains and in the finest interstices.<sup>1</sup>

The soil atmosphere is continually in motion, following with more or less decided lag the barometric changes in the atmosphere above the soil. Moreover, the chemical and physical processes continually taking place in the soil involve the absorption or the formation of free carbonic acid, and it seems probable that all rain water penetrating the soil gives up some oxygen to the soil atmosphere. The bacteria and lower life forms are necessarily undergoing changes continually. In fact all components of the soil are continually undergoing, or are involved in, changes of one kind or another.

It is certain that investigation of the various motions and changes taking place in the soil is quite as important as investigation of the soil components, and that no clear idea of the chemistry of the soil can be obtained without it. The development of a rational practice of soil control is possible only when the soil is regarded from a dynamic viewpoint.

<sup>1</sup> Leather, however, thinks the water returns from only a limited depth, some 5-7 feet; see, *The loss of water from soil during dry weather*, by J. Walter Leather, Memoirs of the Department of Agriculture, Agricultural Research Institute, Pusa, India, Chemical series, 1, 79-116, (1908). Dr. George N. Coffey has called the author's attention to some observations in Western Kansas, where a prolonged drought had dried the soil to a considerable depth. A fairly heavy rain wetted the soil to less than two feet from the surface, and practically all of this moisture had returned to the surface and evaporated within a few days. Such special cases as these, however interesting in themselves, are even less so than the normal cases in humid areas, where a part of the water passes through the soil as seepage, the larger portion returning to the surface, sometimes through distances of many feet.

## Chapter VI.

### THE FILM WATER.

When a relatively small quantity of water is added to an absolutely dry soil or other powdered solid, there is some shrinkage in the apparent volume of the soil or powder. The water spreads over the surfaces of the solid particles in a film, and a rise in temperature shows that a noticeable energy change accompanies the formation of the film.<sup>1</sup> With further increments of water the apparent volume of the soil increases until a maximum is reached. The water content at which this maximum volume of soil can be attained is a definite physical characteristic for any given soil. What is popularly known as the "optimum water content" corresponds to this critical content.<sup>2</sup> It is the point at which further additions of water will not increase the thickness of the moisture film on the soil grains, but will give free water in the soil interstices. Just as the apparent volume of a given mass of soil varies with the water content, and reaches a maximum at a critical moisture content, so do all the physical properties vary and have either a maximum or minimum value

<sup>1</sup> See, in this connection, Energy changes accompanying absorption, by Harrison E. Patten, Trans. Am. Electrochem. Soc., 11, 387-407, (1907); see also the recent valuable research, Les dégagements de chaleur qui se produisent au contact de la terre sèche et de l'eau, par A. Muntz et H. Gaudechon, Ann. sci. agron. (3), 4, II, 393-443, (1900), where it is shown that probably a part of the heat is due to chemical combination between the water and the other soil components. To quote, "Ces diverses observations nous conduisent à penser, sans nous en donner toutefois la preuve absolue, que la fixation de l'eau sur les éléments terreux très fins et sur les matériaux organisés, est tout au moins, en partie, attribuable à une combinaison chimique qui se manifeste non seulement par un fort dégagement de chaleur, mais aussi par la soustraction de l'eau à des substances aux-quelles elle semble chimiquement liée."

<sup>2</sup> The moisture content and physical condition of soils, by Frank K. Cameron and Francis E. Gallagher, Bull. No. 50, Bureau of Soils, U. S. Dept. of Agriculture, 1908. See also Über physikalische Bodenuntersuchung, von H. Rodewald, Schriften Naturwiss. Vereins Schleswig-Holstein, 14, 397-399, (1909).

at this same critical moisture content. Thus the apparent specific gravity of a soil reaches a minimum, the force required to insert a penetrating tool becomes a minimum, while the rate at which a soil warms up reaches a maximum,<sup>1</sup> and the ease with which aeration takes place reaches a maximum. In fine, this critical water content is that at which the soil can be brought into the best possible physical condition for the growth of crops. The practical significance of the optimum water content is far greater than would be supposed from the attention given it hitherto by students of the soil. It is the content of soil water which the greenhouse man should strive to maintain, and which the irrigation farmer should seek to provide, instead of the over-wetting so common to the practice of both. In general farming it is that moisture content at which the farmer will attain the best results in plowing and cultivating, and attain these results most readily.

With additions of water beyond the critical point, there is a presence of free water in the soil interstices accompanied by important changes in the soil structure. With continued additions, there is a more or less rapid decrease in the apparent volume; there is a tendency for the soil aggregates to break down and the "crumb structure" so greatly desired by agriculturists is less and less readily obtained, and working of the soil tends in some cases to produce that phenomenon known as "puddling." However desirable the property of puddling may be to the potter or the brick maker, to the farmer it is a bane to be avoided above all things. To overcome it requires his best skill, and it usually takes several years of patient effort to restore a puddled soil to good tilth.

The force with which the film water is held against the soil grains has not been determined as yet with any degree of precision, but it is certainly very great. If a soil be saturated, that is, if so much water be added that further additions will cause a flow of free water, and the soil be then submitted to some mechanical device for abstracting the water, the moisture content

<sup>1</sup> Heat transference in soils, by Harrison E. Patten, Bull. No. 59, Bureau of Soils, U. S. Dept. Agriculture, 1909.

of the soil can be readily diminished to the critical water content; but to diminish it further by mechanical means is not easy. The tenacity with which film water is held by the soil grains has been shown in several ways. In one of these, for instance, a semi-permeable membrane was precipitated in the walls of a porous clay cell, which was then filled with sugar solution having an osmotic pressure of about 35 atmospheres. When this cell was buried in a soil having a moisture content above the optimum, water flowed into the cell. On the contrary, when the cell was buried in another sample of the same soil having a moisture content well below the optimum, there was a marked flow of water from the cell. It would appear, therefore, that the attraction between the soil grains and the film-forming water was certainly greater than the solution pressure of the sugar.<sup>1</sup> Again, by whirling wetted soils in a rapidly revolving centrifuge,<sup>2</sup> fitted with a filtering device in the periphery, and developing a force equivalent on the average to 3,000 times the attraction of gravitation, the soils could not be reduced below the critical water content. From the results of Lagergren,<sup>3</sup> Young,<sup>4</sup> and Lord Rayleigh,<sup>5</sup> it appears that the force holding a very thin moisture film on the soil grains would be of an order of magnitude from 6,000 to 25,000 atmospheres. This force, however, must greatly decrease with thickening of the film, as is shown by the fact that at the critical moisture content a small further addition of water produces no marked heat manifestation, though making a noticeable difference in the physical properties of the soil.

<sup>1</sup> The chemistry of the soil as related to crop production, by Milton Whitney and Frank K. Cameron, Bull. No. 22, Bureau of Soils, U. S. Dept. Agriculture, 1903, p. 54.

<sup>2</sup> The moisture equivalent of soils, by Lyman J. Briggs and John W. McLane, Bull. No. 45, Bureau of Soils, U. S. Dept. Agriculture, 1907.

<sup>3</sup> Über die beim Benetzen fein verteilter Körper auftretende Wärmetonung, von Lagergren, Bihang till K. sv. Vet.-Akad., Handl., 24, Afd. II. No. 5, (1898).

<sup>4</sup> Hydrostatics and elementary hydrokinetics, George M. Minchin, p. 311, 1892.

<sup>5</sup> On the theory of surface forces, by Lord Rayleigh, Phil. Mag. (5), 30, 285-298, 456-475, (1890).

Therefore, while recognizing that our knowledge of this force still lacks a desirable precision, it is nevertheless clear that the force is very great.

The function of the film water in maintaining the soil structure is undoubtedly important. A soil in good tilth, or good condition for crop growth, shows a peculiar structural arrangement of the individual soil grains or soil particles, which it is very difficult to describe in precise terms, but which is readily recognized in practice. This condition is usually described as a "crumb structure," either because of its appearance or because of the peculiar crumbly feeling which a soil in this condition gives when rubbed between the fingers. The individual grains of soil are gathered into groups or floccules. While other causes may be more or less operative in particular cases, it seems very probable that the film water is primarily the agency holding together the grains in these floccules. The obvious explanation is that the film is exerting a holding power because of its surface tension. It follows, therefore, that anything which affects the surface tension of water should affect the structure of the soil; that is, the flocculation or granulation of the particles. But certain agents which produce respectively flocculation or deflocculation, nevertheless modify the surface tension of the solution in the same direction, and in not widely varying degree. Similar difficulties arise in attempting to correlate "crumbing" phenomena with the viscosity of the film water,<sup>1</sup> and it must be admitted frankly that present views on this subject are very unsatisfactory, and that more careful investigation is urgently needed on this fundamental and important problem. Not only is the absence of a satisfactory theory embarrassing in considering the problems of soil structure and a rational control, but the difficulties are no less in the equally important problems of the movement of film moisture, and the distribution of moisture in a soil.

<sup>1</sup> Equally unsuccessful is the attempt to correlate flocculating agents with changes in the density of water. See, The condensation of water by electrolytes, by F. K. Cameron and W. O. Robinson, Jour. Phys. Chem., 14, 1-11, (1910).

The movement of moisture into a soil from an illimitable supply is a comparatively simple phenomenon, controlled by a rate law which may be expressed by the equation  $y^n = kt$  when  $y$  is the distance through which the movement has taken place;  $t$  is the time, and  $k$  and  $n$  are characteristic constants for the particular soil and solution.<sup>1</sup> This expression may be more readily recognized as a rate formula when written  $dy/dt = Ay^m$ , where  $A$  and  $m$  are constants for the particular system. The first form of the equation promises to be the more useful. This formula also describes the rate of advance of a dissolved substance into the soil.

Owing to irregularities in the soil column this equation is more readily studied with capillary tubes or with such absorbents as filter-paper or blotting paper. The following tables will, however, give an idea as to its validity for soils.

ALLUVIAL SOIL, GILA RIVER.<sup>2</sup>

Time, $t$ min.	Height, <sup>3</sup> inches	$k$ ( $n = 1.86$ )
2	1.5	1.05
5	2.4	1.02
10	3.6	1.08
15	4.3	1.01
30	6.3	1.05
60	9.2	1.07

DISTILLED WATER IN PENN. LOAM ( $T = 21^\circ \text{ C.}$ ).

Time, $t$ min.	Height, <sup>3</sup> cm.	$k$ ( $n = 2.25$ )	Time, $t$ min.	Height, <sup>3</sup> cm.	$k$ ( $n = 2.25$ )
1	1.15	1.37	20	3.90	1.07
2	1.51	1.33	30	4.67	1.06
3	1.85	1.33	40	5.39	1.11
4	2.08	1.30	50	5.90	1.09
5	2.28	1.28	60	6.47	1.12
7	2.59	1.21	75	7.20	1.13
10	2.97	1.16	90	8.03	1.21
15	3.47	1.10	105	8.72	1.25

<sup>1</sup> See Bull. No. 30, Bureau of Soils, U. S. Dept. Agriculture, p. 50 *et seq.*; also, The flow of liquids through capillary spaces, by J. M. Bell and F. K. Cameron, *Jour. Phys. Chem.*, 10, 659, (1906); See also, Wo. Ostwald, 2 Supplementheft *Zeitschrift Kolloidchemie*, 1908, 20.

<sup>2</sup> Computed from observations by Loughridge, Report Agr. Expt Sta., University California, 1893-94, p. 93.

INDIGO CARMINE IN PENN. LOAM SOIL ( $T = 21^{\circ}$  C.).

Solution contained 2 grains dye per liter.

Time, $t$ min.	Height, $h$ wet cm	$k$ for water ( $n = 2.283$ )	Height colored cm	$C$ for dye ( $n = 2.283$ )
1	1.28	1.75	0.64	0.37
2	1.67	1.59	0.60	0.39
3	2.05	1.68	0.62	0.37
4	2.26	1.56	0.62	0.37
5	2.39	1.56	1.02	0.21
7	2.74	1.38	0.62	0.37
10	3.20	1.40	0.62	0.37
15	3.72	1.29	0.62	0.37
20	4.28	1.32	1.92	0.22
30	5.10	1.31	0.62	0.37
40	5.77	1.29	2.69	0.23
50	6.41	1.26	3.20	0.28
60	6.90	1.29	0.62	0.37
75	7.46	1.23	0.62	0.37
90	8.74	1.19	3.59	0.20
105	9.00	1.33	0.62	0.37

It has also been shown repeatedly by experiment that the movement of moisture is relatively rapid when the moisture content of the soil is above the optimum, but that the movement is exceedingly slow when the soil has a lower water content than the optimum; that is, the point at which the water is entirely in the form of film water. For instance, if a moderately wet sample of soil be brought into intimate contact with an air-dry sample of the same soil, there will, at first, be a relatively rapid movement of the moisture, but as soon as the wetted portion has been brought to the "optimum" condition, no further movement can be detected, although the experiment has been tried of leaving such samples together for months and with a difference of water content amounting, in the case of clay soils, to 15 or 20 per cent. Since the drought limit, or the soil moisture content at which plants wilt, is, for most soils, considerably below the optimum water content, the movement of film water is obviously a problem of the first importance from a practical point of view as well as of the highest theoretical interest.

The movement of water vapor, or its distillation from place to place in the soil, is another problem often confused with the above. Its importance is not yet clear, although according to

some investigators<sup>1</sup> it would appear that the addition of soluble fertilizer salts by causing a lowering of the vapor pressure of the water induces a distillation to that region from other regions of the soil as well as from the atmosphere above. This brings up the problem of the diffusion of water and other vapors through the soil. It has been shown that the soil "plug" retards the rate at which diffusion takes place but induces no other effect in the ordinary phenomenon of free diffusion. This fact is obviously of the first importance in the theory of mulches, but requires no further consideration here.<sup>2</sup>

<sup>1</sup> Sur la diffusion des engrains salins dans le terre, par Muntz et Gaudechon, Comptes rendus, 148, 253-258, (1909).

<sup>2</sup> See, Contribution to our knowledge of the aeration of soils, and Studies of the movement of soil moisture, by Edgar Buckingham, Bull. Nos. 25, 1904, and 33, 1907, Bureau of Soils, U. S. Dept. of Agriculture

## Chapter VII.

### THE MINERAL CONSTITUENTS OF THE SOIL SOLUTION.<sup>1</sup>

The mineral constituents of the soil are products of the disintegration, degradation and decomposition of rocks. The decomposition products are mainly silica in the form of quartz, ferruginous material consisting of more or less hydrated ferric oxide and alumina, and hydrated aluminum silicate. The ferruginous material, being deposited or formed in the soil in a very finely divided condition, frequently coats the soil fragments to such an extent as completely to mask their true character. But if a soil be thoroughly shaken with water, and especially in the presence of some deflocculating agent such as a slight excess of ammonia, as in the ordinary preparation of a soil sample for mechanical analysis<sup>2</sup> the coating material is generally removed quite readily, and the mineral particles appear as fragments and splinters of the ordinary rock-forming minerals. Sometimes these fragments are more or less worn and rounded at the edges, showing mechanical abrasion or solvent action; sometimes they show evidences of partial alteration and decomposition; but surfaces of the unaltered mineral individuals always are found. These unaltered minerals occur as fragments of all sizes, and are to be found in the sands, silts, and presumably in the clays. As might be anticipated, the minerals other than quartz generally show a tendency to segregate in the finer mechanical separations of the soil. The presence of these unaltered mineral fragments in the clays has so far defied direct experimental proof because of the limitations of the microscope, but from chemical reasoning and *a priori* considerations there

<sup>1</sup> For a more detailed discussion and citations of the literature, see The mineral constituents of the soil solution, by Frank K. Cameron and James M. Bell, Bull. No. 30, Bureau of Soils, U. S. Dept. Agriculture, 1905.

<sup>2</sup> Centrifugal methods of mechanical soil analysis, by L. J. Briggs, F. O. Martin and J. R. Pearce, Bull. No. 24, Bureau of Soils, U. S. Dept. Agriculture, 1904.

can be but little doubt that they exist in the clays as in the coarser separations.<sup>1</sup>

The minerals to be anticipated in the soil are those commonly occurring in the rocks; but as a result of the action of mixing and transporting agencies, a soil normally contains minerals from rocks other than those from which it is primarily derived.

It would hardly be fair to regard a beach sand, for instance, as a normal soil. Yet it is surprising how many minerals other than quartz can usually be found even in a beach sand. Opinions may differ as to just what are the common rock-forming minerals, and perhaps no two mineralogists or petrographers would give identical lists, but there are a number of minerals which would appear undoubtedly in every list, and these would be found generally in any soil. Again, it might happen that in any given sample of soil, no pyroxene, for instance, could be found; but experience shows that it would never happen in such a case that no amphibole, chlorite, serpentine, or other ferromagnesian silicates would be present. However distinct these minerals cited may be from each other morphologically or optically, they are much the same in their chemical characteristics, their solubilities and their reactions with water and such dilute solutions as exist in the soil. Hence from the point of view of the soil chemist they may be considered for all practical purposes varieties of one and the same mineral species. Consequently an important result of researches on the minerals of the soil is the generalization that soils are far more heterogeneous than are rocks, and that *practically every soil contains all the common rock-forming minerals.*<sup>2</sup>

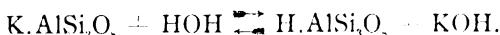
It is not difficult to account for the heterogeneity of the mineral content of the soil. Many of our rocks are reconsolidated

<sup>1</sup> See, 'The mineral composition of soil particles,' by G. H. Failyer, J. G. Smith and H. R. Wade, Bull. No. 54, Bureau of Soils, U. S. Dept. Agriculture, 1909. Recent improvements in microscope methods make it possible to identify without serious trouble the mineral content of silts with a diameter as low as 0.005 mm., and many even of the clay particles have recently been determined with satisfactory accuracy.

<sup>2</sup> See Bull. No. 30, Bureau of Soils, U. S. Dept. Agriculture, 1905, p. 9.

soils, and the alternating formation of rock and soil from the same materials is probably an agency, in some part at least, in the mixing of soil material. The action of water in carrying off and transporting surface material and in gullying and eroding sloping surfaces is probably a large factor. But this agency, like the first, is rather restricted and localized. Just as important as a mixing agency is the wind. This, unlike water, works uphill as well as down, and is more or less in action at all times, continually transporting soil material from place to place. Wind-borne dust on roofs of dwellings, on rocky mountain tops and similar places, where it could have been brought by no other agency than the wind, is sometimes found supporting vegetation. Many chemical and mineralogical analyses of wind-borne dust obtained from various locations show it to have generally the same essential characteristics as ordinary soils.

Aside from the quartz and ferruginous materials mentioned above, the major part of the soil minerals are silicates, ferrosilicates, alumino-silicates or ferro-alumino-silicates, of the common bases, sodium, potassium, calcium, magnesium, and ferrous iron. Other bases, such as lithium, barium, or the heavy metals may occasionally be present in appreciable amounts as may other types of silicates, or other mineral salts, but these may be regarded as more or less incidental and rarely affecting in any essential way the general character of the soil mass. These silicates or silico minerals are all somewhat soluble in water, and being salts of weak acids with strong bases, are greatly hydrolyzed. A convenient illustration is afforded by the well-known rock and soil mineral, orthoclase. Assuming its type formula, the reaction with water may be represented,

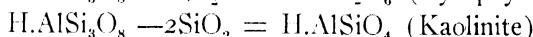


Under ordinary soil conditions, with a relatively large proportion of carbon dioxide in the soil atmosphere, the potash formed would be more or less completely transformed to the bicarbonate,



Confirmation of this view is afforded by the natural associations and known alteration products of orthoclase.

The acid of the formula  $H.AlSi_3O_8$  is not known and is probably entirely unstable under ordinary conditions, and breaks down with the separation of silica, to form the minerals pyrophyllite, kaolinite or kaolin, and diasporite according to the following equations:



All three of these minerals and their corresponding salts have been found in nature as alteration products of orthoclase. It is probable that, under soil conditions, the principal metamorphic product of feldspar is kaolin (or kaolinite when it is crystalline), hydrated aluminum oxide being of much less importance<sup>1</sup> and pyrophyllite of doubtful occurrence. A still more interesting case, perhaps, because of the well recognized tendency of magnesium salts to form basic compounds, is the alteration of pyroxene, amphibole and olivine with the formation of a chlorite or serpentine, common associations in nature, which may be represented



It is tacitly assumed in the foregoing statements that the reaction between a silicate mineral and water is a reversible reaction. This is not definitely known to be the case, for the formation of the ordinary silicate rock-forming minerals in the wet way at ordinary temperatures has as yet been realized in only a few cases. The assumption has, however, some experimental support. Minerals have been often made in the wet way at somewhat elevated temperatures, especially interesting cases in this connection being the formation of orthoclase by Friedel and Sarasin<sup>2</sup> at slightly elevated temperatures, and the formation of

<sup>1</sup> See Ueber die Bildung von Bauxit und verwandte Mineralien, von A. Liebrich, Zeit. prakt. Geol., 1897, 212-214.

<sup>2</sup> Sur la reproduction par voie aqueuse du feldspath orthose, par Friedel et Sarasin, Comptes rendus, 92, 1374, (1881).

zeolites by Gonnard<sup>1</sup> and by Doroshevskii and Bardt,<sup>2</sup> and the formation of apatite by Weinschenk.<sup>3</sup> Feldspars and zeolites are common natural associations, it being generally conceded that zeolites are alteration products of the feldspars through the action of water; but Van Hise<sup>4</sup> has pointed out that under conditions of weathering such as would obtain in the soil, the tendency is for the zeolites to alter to feldspars. Wöhler's classical experiment of recrystallizing apophyllite from hot water<sup>5</sup> is significant, for only the products of hydrolysis should be obtained if there is an irreversible reaction between the mineral and water. Lemberg found that leucite ( $KAlSi_2O_6$ ) when treated with an aqueous solution containing 10 per cent. or more of sodium chloride, was partially transformed to analcime ( $NaAlSi_2O_6 \cdot nH_2O$ ), potassium chloride being formed at the same time. The reverse reaction was also realized, that is, the partial conversion of analcime to leucite by treatment with a solution of potassium chloride, and similar transformations were carried out with the feldspars.<sup>6</sup> Lemberg's experiments are of especial value as they were carried out at ordinary as well as at high temperatures. It appears probable, therefore, that the hydrolysis of a silicate of the alkalis or alkaline earths is a reversible reaction. It should be noted, however, that Kahlemburg and Lincoln<sup>7</sup> have shown that probably, in very dilute solutions of alkali silicates, the hydrolysis is

<sup>1</sup> Note sur une observation de Fournet, concernant la production des zéolites à froid, par F. Gonnard, Bull. Soc. min. France, 5, 267-269, (1882); Jährb. Min., 1884, I, Ref. 28.

<sup>2</sup> Metathetical reactions with artificial zeolites, by A. Doroshevskii and A. Bardt, Jour. Russ. Phys. Chem. Soc., 42, 435-42 (1910). Chem. Zentr., 1910, II, 68.

<sup>3</sup> Beiträge zur Mineralsynthesen, von E. Weinschenk, Zeit. Kryst., 17, 489-504, (1890).

<sup>4</sup> U. S. Geol. Surv. Monograph, 47, A treatise on metamorphism, by Charles R. Van Hise, 1904, p. 333.

<sup>5</sup> Jahresb. Fortschr. Chemie Liebig and Kopp, 1847-48, 1262; note.

<sup>6</sup> Ueber Silicatumwandlungen, von J. Lemberg, Zeit. deutsch. geol. Ges., 28, 519-621, (1876); Inaug. diss. Dorpat, 1877; Bied. Centbl., 8, 567-577, (1879).

<sup>7</sup> Solutions of silicates of the alkalis, by L. Kahlemburg and A. T. Lincoln, Jour. Phys. Chem., 2, 77-90, (1898).

practically complete and the silica is nearly all present as colloidal silica and not as silicic acid. Nevertheless at higher concentrations silicates are formed, and there is abundant evidence in nature that the alumino- or ferro-silicates are reacting with bases to form salts, for example such as the micas.<sup>1</sup> If the hydrolysis were quite complete, it would appear to follow that the reaction between water and the silicate is irreversible. In that case it is difficult to see how any silicate mineral could persist in the soil for any length of time, and all soils should soon become sterile wastes composed essentially of quartz, kaolin and ferruginous oxides. It has been suggested that the original mineral particles are protected from decomposition by the formation of a coating "gel." That is, that silica, alumina, ferruginous or other materials result from the decomposition of the minerals in a jelly-like form on the surface of the soil grains, protecting them from further action of the soil solution.<sup>2</sup> If diffusion can take place through the gel, solution and hydrolysis of the mineral would proceed, although the presence of the gel would probably retard the rate of the reaction. If it be postulated, however, that diffusion through the gel does not take place, the minerals of the soil can have no influence on the composition of the soil solution, which is an unthinkable alternative. The presence of such gels in the soil has frequently been assumed, but satisfactory proof is generally wanting.

In general, the same kind of considerations developed for orthoclase hold for the other soil minerals. If minerals of this character be pulverized or ground reasonably fine and then be

<sup>1</sup> Van Hise, loc. cit., p. 693.

<sup>2</sup> A gel is a jelly-like substance, apparently continuous, which forms either by the settling from suspension in a liquid of very fine particles which then become aggregated; or, is formed by the evaporation of a liquid containing fine particles in suspension until the quantity of liquid remaining is just sufficient to serve as a cementation medium holding the suspended particles together in a semi-rigid mass. For an experimental demonstration of the formation of such a gel, see, The effect of water on rock powders, by Allerton S. Cushman, Bull. No. 92, Bureau of Chemistry, U. S. Dept. Agriculture, 1905.

shaken with distilled water which has been previously boiled to eliminate the dissolved carbon dioxide, the resulting solution will give an alkaline reaction with such indicators as phenolphthalein or litmus.<sup>1</sup> If a soil be shaken up thoroughly with water, the resulting solution filtered free of suspended matter, as by passing through a Pasteur-Chamberland bougie, and then boiled to eliminate the carbon dioxide, in the vast majority of cases the solution will also give an alkaline reaction with phenolphthalein or litmus. The waters of most of our springs, ponds, creeks or rivers being natural soil solutions, give an alkaline reaction after boiling.

But the mineral content of these natural waters varies greatly. These waters are composed in part of the "run-off," in part of a portion of the "cut-off" waters, described above. This portion of the cut-off, normally, in passing through the soil goes mainly through the larger interstices. It is not long in contact with the individual soil particles and floccules, and because diffusion of dissolved mineral substances is quite slow, especially in dilute solutions, it takes up but little mineral matter from such aqueous films as it may intercept.

A different state of things exists with that portion of the cut-off water which returns towards the surface by reason of capillary forces, to form the great natural nutrient medium for plants. This water is moving over the soil particles in filius, and with slowness. It is long in contact with successive fragments of any particular mineral and all the different minerals making up the soil. Consequently, it tends towards a saturated solution with respect to the mineral mass; and it follows that if every soil contains all the common rock-forming minerals, every soil should give the same saturated solution, barring the presence of

<sup>1</sup> In making such experiments in the laboratory or in lecture demonstrations, it is well to have the mass of water large in comparison with the mass of powdered mineral or rock; otherwise secondary adsorption effects may occur and obscure the results of the hydrolysis.

disturbing factors.<sup>1</sup> Disturbing factors, however, enter into all cases under field conditions, such for instance as the presence of some uncommon or unusual mineral in appreciable amounts, differences in temperature, surface effects, or extraneous substances. These will be considered later, but another disturbing factor requires immediate consideration.

In every soil, varying proportions of the soluble mineral constituents are present otherwise than as definite mineral species; that is, they are present as solid solutions, or absorbed on the soil grains or perhaps absorbed in some other manner. The concentration of the liquid solution in contact with a solid solution or complex of absorbent and absorbed material is dependent upon the relative masses of solution and solid. Thus, the concentration of a solution with respect to phosphoric acid, when brought into contact with so-called basic phosphates of lime or iron, is dependent in a marked way upon the proportion of solution to solid.<sup>2</sup> Consequently it is to be expected that an aqueous extract of a soil will vary in concentration with the proportion of water used; and that with the same proportion of water, different soils or different samples of the same soil will yield different concentrations.

How far absorbed mineral constituents affect the solubility of the definite minerals in the soil or influence the concentration of the soil solution, it is not possible to predict with any approach to certainty. Those soils which hold the most moisture are generally the best absorbers. Moreover, the soluble mineral constituents of the soil, for instance potassium or phosphoric acid, are absorbed to a very high degree from dilute

<sup>1</sup> Feldspars certainly, and phosphorites possibly, are mineral components of the soil; and these substances when ground sufficiently fine have been added to soils with sometimes an increased production of crop. Other minerals, such as leucite, have given similar results. But also apparently pure quartz sand sometimes accomplishes the same results, as for example, in the experiments of Hilgard cited above. It has not been shown, however, that the addition of any of these substances produces an appreciable change in the concentration of the soil solution.

<sup>2</sup>The action of water and aqueous solutions upon soil phosphates, by Frank K. Cameron and James M. Bell, Bull. No. 41, Bureau of Soils, U. S. Dept. of Agriculture, 1907.

solutions. Consequently it is to be expected that variations in the concentration of the natural soil solution would be less than in aqueous extracts, when there is employed a constant and relatively large proportion of water to soil. These considerations are of great theoretical importance since they appear to negative the possibility of getting, with present experimental resources, any *exact* knowledge of the concentrations of the mineral constituents in the soil solution when the soil is in condition to grow the common crop plants. Moreover, they furnish a guide to the limitations which must be recognized in attempting to postulate what these concentrations may be on the basis of analytical data obtained from aqueous soil extracts.

Many attempts have been made to extract the solution naturally existing in the soil and to analyze it. The results obtained have not been very satisfactory, owing mainly to the mechanical difficulties involved. As pointed out above, the solution in a soil under suitable conditions for crop growth is held by a force of great magnitude. Nevertheless, by using powerful centrifuges, with saturated soil, it has been possible to throw out the excess of solution over the critical water content of the soil. In this way small quantities, generally a very few cubic centimeters at a time, have been obtained. The analysis of a few cubic centimeters of a very dilute solution is in itself difficult, involving necessarily more or less uncertainty as to the absolute value of the results. Nevertheless, the concentration of the soil solutions thus obtained, with respect to phosphoric acid and potash, varied but little for soils of various textures from sands to clays, and the variations observed could not be correlated with the known crop-producing power of the soils. The average concentrations of the soil solutions thus obtained lies in the neighborhood of 6-8 parts per million (p.p.m.) of solution for phosphoric acid ( $P_2O_5$ ) and 25-30 parts per million for potash ( $K_2O$ ).<sup>1</sup> In the following table are given the results obtained

<sup>1</sup> In this connection it is interesting to note that recent investigations on the proportions of phosphoric acid, potassium and nitrates in cultural solutions best adapted to the growth of wheat, give the same ratio of phosphoric acid to potassium as the figures just cited show to exist normally in the soil solution.

by analyzing solutions extracted from different samples of loams and sands by means of a centrifuge. The crop growing on these soils and the crop condition at the time the samples were collected are given in the table, and the percentages of water in the samples when placed in the centrifuge are also given.

ANALYSIS OF SOIL SOLUTION REMOVED FROM FRESH SOILS  
BY THE CENTRIFUGE.

Soil	Crop	Condition of crop	Per cent moisture.	Parts per million of solution		
				PO <sub>4</sub>	Ca	K
Leonardtown loam .....	Wheat	Good	22.0	6	17	22
Leonardtown loam .....	Wheat	Poor	25.2	10	9	19
Leonardtown loam .....	Wheat	Good	17.6	8	22	38
Sassafras loam .....	Clover	Good	19.7	5	18	19
Sassafras loam .....	Corn	Medium	17.5	8	13	36
Sassafras loam .....	Corn	Medium	18.3	8	83	25
Sassafras loam .....	Wheat	Good	18.8	7	44	34
Sassafras loam .....	Wheat	Poor	20.0	7	27	24
Sassafras loam .....	Corn	Good	17.3	8	24	25
Norfolk sand .....	Forest	Poor	10.0	5	18	31
Norfolk sand .....	Corn	Good	11.9	11	36	31
Norfolk sand .....	Wheat	Good	10.7	18	45	31
Norfolk sand .....	Wheat	Poor	11.2	8	38	24
Norfolk sand .....	Corn	Medium	10.6	9	65	35

The concentrations of the solutions obtained from the samples do not justify any correlation with the crop-producing power of the soils, nor with the texture of the soils. The wide variation in the concentrations with respect to calcium is probably due to the fact that all of the samples came from fields which had been limed, some quite recently, and that the content of carbon dioxide in the different samples varied. It is of special interest to note that the content of calcium in the solutions does not show any obvious relation to the content of phosphoric acid.<sup>1</sup>

An effort has been made to ascertain the mineral concentration of soil solutions as they occur naturally in the field. Be-

<sup>1</sup> For the literature of the earlier work on the composition of aqueous extracts of soils, see: How crops feed, by Samuel W. Johnson, 1890, p. 309 *et seq.*; see also, On the analytical determination of probably available "mineral" plant-food in soils, by Bernard Dyer, Jour. Chem. Soc., 65, 115-167, (1894); and Soils, by E. W. Hilgard, 1906, p. 327 *et seq.*

cause of the practical impossibility of extracting the actual soil solution, an empirical method was employed. Areas were selected where good and poor crops were growing near each other on the same soil types, and preferably in the same field. Samples of soil from under these crops were taken at several intervals during the growing season, quickly removed to a nearby laboratory, shaken thoroughly with distilled water in the proportion of one part of soil to five parts of water, allowed to stand twenty minutes and the supernatant solution passed through a Pasteur-Chamberland filter.<sup>1</sup>

As has been pointed out above, the aqueous extract of a soil thus arbitrarily prepared has no definite or causal relation to the soil solution in the field. It is certain that the solutions would not generally be the same. It should also be emphasized that such a procedure can not, as some investigators have assumed, afford a criterion between soluble and insoluble salts in the soil, else the proportion of water to soil used above some minimum would be immaterial as far as the amounts which go into solution are concerned. The proportion of water to soil is not immaterial, however, considering the chemical nature of the soil components and the results of experiment. Consequently, it is clear that the concentration of the soil solution is not simply the ratio of the amounts found in the aqueous extract, to the percentage of moisture in the soil, but something quite different.

Artificial solutions prepared in the manner described above should, however, furnish evidence as to whether or not there are recognizable differences in the soluble mineral constituents of good and poor soils respectively; and if such differences exist, whether they are consistent. That is to say, if the more productive soils also uniformly yield aqueous extracts of a higher concentration, then it would be a fair inference that their natural soil solutions are maintained at a higher concentration than in the less productive soils.

<sup>1</sup> Capillary studies and filtration of clays from soil solutions, by Lyman J. Briggs and Macy H. Lapham, Bull. No. 19, Bureau of Soils, U. S. Dept. Agriculture, 1902; Colorimetric, turbidity and titration methods used in soil investigations, by Oswald Schreiner and George H. Failyer, Bull. No. 31, Bureau of Soils, U. S. Dept. Agriculture, 1906.

Results obtained for several localities and several crops, taken from the original records, are given in the following tables.<sup>1</sup>

WATER SOLUBLE CONSTITUENTS OF SOIL.

Locality, Salem, N. J. Soil type, Norfolk sand. Crop, wheat.  
Yield, good.

Date	Depth inches	Moisture content Per cent.	Parts per million of oven-dried soil		
			Phosphoric acid ( $\text{PO}_4$ )	Calcium (Ca)	Potassium (K)
March 10.....	0-12	13.2	12	5	12
	12-24	11.5	7	5	16
June 8 .....	1-24	4.3	4	14	13
June 13 .....	1-24	4.6	5	13	17
June 19 .....	1-24	9.6	2	14	24

Locality, Salem, N. J. Soil type, Norfolk sand. Crop, wheat.  
Yield, poor.

Date	Depth inches	Moisture content Per cent.	Parts per million of oven-dried soil		
			Phosphoric acid ( $\text{PO}_4$ )	Calcium (Ca)	Potassium (K)
April 3.....	0-12	12.0	11	5	32
	12-24	12.0	10	3	22
June 16 .....	1-24	9.3	4	29	20

Locality, Salem, N. J. Soil type, Sassafras loam. Crop, wheat.  
Yield, medium.

Date	Depth inches	Moisture content per cent.	Parts per million of oven-dried soil		
			Phosphoric acid ( $\text{PO}_4$ )	Calcium (Ca)	Potassium (K)
March 10.....	0-12	23.2	19	10	8
	12-24	21.6	11	10	14
March 14.....	0-12	22.3	18	8	18
	12-24	20.2	15	12	21
March 20.....	24-36	20.3	18	17	16
	0-12	19.3	7	10	21
	12-24	18.6	4	11	21
June 16 .....	24-36	12.6	5	12	21
	1-24	22.5	4	14	23

<sup>1</sup> The chemistry of the soil as related to crop production, by Milton Whitney and F. K. Cameron, Bull. No. 22, Bureau of Soils, U. S. Dept. Agriculture, 1903.

Locality, Salem, N. J. Soil type, Sassafras loam. Crop, grass.  
Yield, fair.

Date	Depth inches	Moisture content per cent.	Parts per million of oven-dried soil		
			Phosphoric acid ( $\text{PO}_4$ )	Calcium (Ca)	Potassium (K)
March 10 . . . . .	0-12	25.0	13	28	18
	12-24	23.8	7	26	13
	24-36	19.9	16	8	15
March 14 . . . . .	0-12	25.8	21	12	21
	12-24	23.1	8	12	15
	24-36	21.8	9	15	21
March 31 . . . . .	0-12	23.0	11	23	43
	12-24	21.6	8	20	34
April 2 . . . . .	0-12	24.8	8	16	41
	12-24	24.0	6	21	38
	24-36	21.4	3	11	25

Locality, Salem, N. J. Soil type, Sassafras loam. Crop, wheat.  
Yield, good.

Date	Depth inches	Moisture content per cent.	Parts per million of oven-dried soil		
			Phosphoric acid ( $\text{PO}_4$ )	Calcium (Ca)	Potassium (K)
March 17 . . . . .	0-12	22.0	8	6	10
	12-24	18.1	8	15	14
March 17 . . . . .	0-12	18.3	10	15	Lost
	12-24	18.1	9	24	25
March 24 . . . . .	0-12	24.7	14	12	30
	12-24	22.3	8	11	38
March 26 . . . . .	0-12	23.4	4	16	16
	12-24	23.9	12	16	20
	24-36	22.4	8	3	21
April 2 . . . . .	0-12	25.6	8	16	30
	12-24	24.4	8	17	47
	24-36	21.6	8	11	38
June 5 . . . . .	0-12	5.2	14	51	23
	12-24	8.0	15	55	32
June 8 . . . . .	1-24	10.6	2	20	13
June 11 . . . . .	1-24	15.5	6	26	14
June 13 . . . . .	1-24	8.2	6	19	22
June 16 . . . . .	1-24	15.0	5	21	19
June 17 . . . . .	1-24	10.6	7	63	17

Locality, Salem, N. J. Soil type, Sassafras loam. Crop, clover.  
Yield, fair.

Date	Depth inches	Moisture content per cent.	Parts per million of oven-dried soil		
			Phosphoric acid ( $\text{PO}_4$ )	Calcium (Ca)	Potassium (K)
March 20.....	0-12	20.8	5	15	32
	12-24	20.2	5	15	27
	24-36	18.6	5	12	36
March 26.....	0-12	26.8	9	31	20
	12-24	22.9	8	20	18
	24-36	22.5	4	14	20
June 6 .....	0-12	8.1	8	16	17
	12-24	12.7	9	18	20

Locality, St. Marys, Md. Soil type, Leonardtown loam. Crop, wheat.  
Yield, good.

Date	Depth inches	Moisture content per cent.	Parts per million of oven-dried soil		
			Phosphoric acid ( $\text{PO}_4$ )	Calcium (Ca)	Potassium (K)
April 27.....	0-12	21.8	5	10	12
	12-24	21.3	4	7	10
April 29.....	0-12	22.2	8	15	52
	12-24	21.8	4	11	38
May 1.....	0-12	22.4	7	14	23
	12-24	21.8	7	8	30
May 1.....	0-12	17.0	5	16	25
	12-24	21.0	5	7	19
May 9.....	0-12	15.0	13	34	28
	12-24	15.9	9	17	26
May 15.....	0-12	14.2	3	14	24
	12-24	19.9	4	13	25
August 14.....	0-24	15.0	6	11	13
August 15.....	0-24	15.7	5	3	17
August 15.....	0-24	16.4	8	15	15

## THE MINERAL CONSTITUENTS OF THE SOIL SOLUTION 45

Locality, St. Marys, Md. Soil type, Leonardtown loam. Crop, wheat.  
Yield, poor.

Date	Depth inches	Moisture content per cent.	Parts per million of oven-dried soil		
			Phosphoric acid ( $\text{PO}_4$ )	Calcium (Ca)	Potassium (K)
May 14.....	0-12	14.7	5	8	35
	12-24	19.9	4	4	30
May 23 .....	0-12	7.8	4	7	22
	12-24	14.9	4	11	23
August 14.....	0-24	16.0	4	4	16
	0-24	19.5	6	4	13

Locality, St. Marys, Md. Soil type, Leonardtown loam. Crop, corn.  
Yield, good.

Date	Depth inches	Moisture content per cent.	Parts per million of oven-dried soil		
			Phosphoric acid ( $\text{PO}_4$ )	Calcium (Ca)	Potassium (K)
May 8 .....	0-12	18.2	9	12	29
	12-24	18.9	10	7	26
May 18 .....	0-12	18.2	3	24	38
	12-24	18.8	6	19	28
August 8 .....	0-24	17.5	7	30	18

Locality, St. Marys, Md. Soil type, Leonardtown loam. Crop, corn.  
Yield, poor.

Date	Depth inches	Moisture content per cent.	Parts per million of oven-dried soil		
			Phosphoric acid ( $\text{PO}_4$ )	Calcium (Ca)	Potassium (K)
May 23 .....	0-12	16.6	5	12	22
	12-24	17.4	6	8	22
August 8.....	0-24	19.9	9	25	20
	0-24	21.6	7	15	13

It will be observed that the results given in the above tables are expressed in parts per million of oven-dried soils, in order to have some definite basis of comparison, and because it was anticipated at the time the investigation was made that larger

quantities of dissolved minerals would be found under the better crops, and *vice versa*. An inspection of the results, however, shows that no such correlation can be made, nor in fact can any consistent correlation be made between the dissolved material and crop, soil type, water content, depth of soil or part of the growing season.<sup>1</sup> It appears, therefore, that in so far as the field method of analyzing an arbitrarily prepared aqueous extract is competent, there is no evidence that there are important characteristic differences in the concentration of the mineral constituents in different soil solutions in the field.

The order of concentration of the soil solution can be approximated from the given data, if the assumption be made that in the preparation of the aqueous extract, soluble mineral constituents are of minor importance, other than the constituents already dissolved in the soil solution. The calculation is very laborious, is not exact, and on account of the assumptions made the actual figures obtained are of no especial value in any particular case. Remembering the method of making up the solutions from which these results were obtained, it would be sufficiently near the truth to assume an average moisture content of 20 per cent., when the figures given here for the soil approximate those which would be obtained for the soil solution. More exact calculations have been made for a large number of such cases, and it has been found from this method of estimation that the average composition with respect to phosphoric acid would be about 6-8 parts per million, and for potash about 25 parts per million, figures which agree with the results obtained for the examination of solutions extracted from saturated soils by means of the centrifuge.

<sup>1</sup> King, however, claims that the concentration of the soil solution with respect to mineral plant nutrients, is higher in the soils of the northern states than in the soils of the South Atlantic states. See: Some results of investigations in soil management, by F. H. King, Yearbook, U. S. Dept. Agriculture, 1903, p. 159-174. Bailey E. Brown has obtained some preliminary results which suggest that there may be seasonal variations with respect to some of the dissolved mineral constituents. See, Annual Report of the Pennsylvania State Experiment Station, 1908-9, pp. 31 *et seq.*

The results given in the foregoing tables were obtained under great difficulties, and in some part the variations they show are undoubtedly due to inevitable inaccuracies of analytical work done under such circumstances. Some of the variations may also be due to the disturbing influences in the soil referred to above. Experience has shown, however, that the preparation of an aqueous extract of the soil of any particular field is by no means a simple matter. Extracts made from samples taken within a few feet of one another frequently show variations of the same order as with samples from entirely different fields, or even soil types. Differences in the preliminary drying out of the sample before the addition of the water, seems to result in the same order of differences as obtained between different soils. In consequence of these facts, and of the further fact that an arbitrary aqueous extract of a soil cannot be assumed to represent in any definite way the natural soil solution, the results of the field examination are inconclusive as to the concentration of the soil solution *in situ*. It is more necessary, therefore, that other lines of evidence should be sought as to the mineral characteristics and concentration of the soil solution. Such a line of evidence is found in certain percolation experiments.<sup>1</sup>

If a solution of a soluble phosphate be percolated through a soil, a part of the phosphate will be removed from the solution and absorbed by the soil; that is, there will be a redistribution of the phosphate between the soil and the water. As the process continues, however, relatively less and less phosphate is absorbed by the soil and the concentration of the percolate becomes more and more nearly that of the added solution. This absorption takes place more or less closely in accordance with the simple law that the absorption of phosphates by the soil, per unit of solution which is percolating, is proportional to the total amount of phosphate which the soil may yet take from that solution if percolated indefinitely. This law is expressed by the equation  $dy/dx = K(A - y)$  where  $y$  is the amount

<sup>1</sup> The absorption of phosphates and potassium by soils, by Oswald Schrejner and George H. Failyer, Bull. No. 32, Bureau of Soils, U. S. Dept. Agriculture, 1906.

absorbed,  $x$  amount of solution that has passed, and  $A$  is the total amount which can ultimately be absorbed by that particular soil from that particular solution.  $K$  is also a characteristic constant. If the percolation be maintained at constant rate, then  $t$ , time, can be substituted for  $x$  and the equation becomes  $dy/dt = K(A - y)$ , the ordinary rate equation for a monomolecular reaction of the first order, whether chemical or physical.

With such absorptions as are involved in soils, a clay exposes a greater amount of absorbing surface than does a loam or sand, and it will show the greatest absorption towards any particular solution, other things being equal. The curve showing the concentration of percolate would lie lower for a clay than for a loam, or for a sand. This is illustrated in the accompanying sketch diagram, where  $y$  represents concentration of percolate and  $t$  represents time.

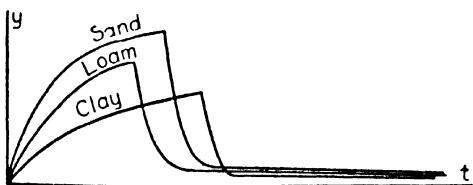


Fig. 1.

If after percolation has proceeded for some time (in some experiments for several weeks and until the soil contained 1 or 2 per cent. of phosphoric acid) pure water be passed through the soil, then, as soon as the previously used phosphate solution has been displaced, the concentration of the percolate drops and continues practically constant for an indefinite period. Moreover, no matter what the soil may be as to texture or composition, the same concentration of percolate is obtained, namely, 6-8 parts per million, the concentration which the soils yielded prior to treatment with the phosphate solution. Similar experiments when the soils were treated with salts of potassium have given like results, although the curves obtained from passing pure water through the soils do not lie quite so close to-

gether; but the concentration of the percolate with respect to potassium generally lies somewhere between 25 and 30 parts per million.

The removal of a soluble constituent from the soil by percolating water appears to be described by a rate equation similar to that given above for absorption. If the rate of percolation be maintained constant this formula is

$$\frac{dx}{dt} = K(B - x)$$

where  $x$  is the amount removed by the percolation, with time  $t$ ,  $K$  is a constant characteristic for the particular system under consideration, and  $B$  is the total amount of the constituent which may ultimately be leached out. In other words, the rate in any particular soil will depend upon the amount of the constituent still absorbed in that soil but has no necessary connection with the rate which would hold for the same amount of the constituent in any other soil.

Theoretically, two consequences follow from this law which require consideration here. The rate at which a constituent is removed gradually becomes less as percolation proceeds. If the soil contains an amount of the constituent approaching the total amount which it can absorb, as for instance is probably the case sometimes when large applications of lime have been made to the soil, the concentration of the percolating solution might be expected to change noticeably. Generally, however, a soil contains nowhere near as much phosphoric acid or potassium as it is capable of absorbing, so that the concentration of the percolating water changes but very little with respect to these constituents. It follows from the equation that if percolation continues uninterrupted, the concentration of the percolate, so far as it is determined by an absorbed constituent, must get less and less until it becomes a vanishing quantity. This state of affairs does not exist in the soil, however, for percolation by pure water does not continue uninterrupted for any length of time. The rise of the capillary water in the soil will, under normal conditions, enable the soil to reabsorb more of the ordinary mineral constituents than is removed by percolating

waters. Further attention will be given the matter in another chapter.

Another but quite different line of evidence as to the probable concentration of the soil solution is furnished by the investigation of the solubility of certain phosphates.<sup>1</sup> It is popularly supposed that when superphosphate containing mono-calcium phosphate,  $\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , is added to a soil there is a more or less permanent increase of readily soluble phosphoric acid in the soil, although a part "inverts" to the somewhat less soluble dicalcium phosphate,  $\text{CaH}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ . Such probably is far from a correct view of what actually takes place. The results obtained by studying the solubility of the different lime phosphates in water at ordinary temperature ( $25^\circ \text{ C.}$ ) can be expressed in a diagram similar to the accompanying sketch, which is much distorted for convenience in lettering. As the diagram indicates, when the concentration of the solution increases with respect to phosphoric acid, the lime is at first less and less soluble until the point represented by *B* is reached, then becomes more and more soluble until the point *D* is reached, from then on becoming less and less soluble, until the solution reaches a

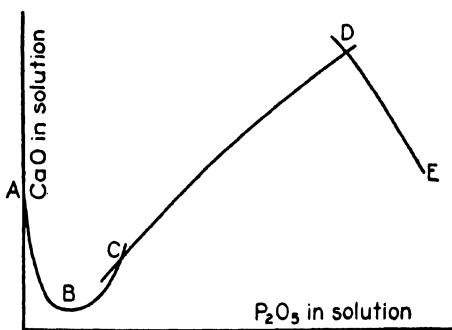


Fig. 2.

syrupy consistency. In contact with all solutions represented by points on the line *DE* the stable solid substance which can

<sup>1</sup> For reference to the literature and detailed discussion see: The action of water and aqueous solutions upon soil phosphates, by F. K. Cameron and J. M. Bell, Bull. No. 41, Bureau of Soils, U. S. Dept. Agriculture, 1907.

exist is mono-calcium phosphate,  $\text{CaH}_4(\text{PO}_4)_2\text{H}_2\text{O}$ . Along the line  $CD$  the only solid which is stable and can continue to persist is the dicalcium phosphate. From the point  $C$  the composition of the stable solid varies continuously with the concentration of the liquid solution. Therefore, these solids form a series varying in composition from pure dicalcium phosphate to pure calcium hydroxide. One of these basic phosphates, as they would ordinarily be called, has a less solubility than any other, as indicated by the point  $B$ . All solutions to the right of the point  $B$  have an acid reaction, while all solutions to the left possess an alkaline reaction. It follows from these facts that if we start with any lime phosphate corresponding to some point to the right of  $B$  and dilute it, or what amounts to the same thing in case it has been added to the soil, if we leach it, phosphoric acid will go into solution more rapidly than will lime until the composition of the residue is that of the basic phosphate stable at  $B$ . Similarly, if we start with a phosphate more basic, lime will be removed more rapidly than phosphoric acid, until the residue has the composition of the phosphate of lowest solubility. From this point, with continued leaching, the lime and phosphoric acid will dissolve in a definite ratio, which ratio is obviously that of the phosphate of least solubility. That is to say, if the leaching process is slow, as would be the case under soil conditions, the solution would have a perfectly definite concentration with respect to lime and phosphoric acid. What the ratio of lime to phosphoric acid may be, is of no particular interest in this connection, but the order of concentration of phosphoric acid is of interest. Owing to serious analytical difficulties, this has not yet been determined with any great precision, but by interpolating on the experimentally determined curve  $AC$ , this concentration is found to be somewhere in the neighborhood of 5-10 parts per million, figures close to those obtained for the concentration of the soil solution with respect to phosphoric acid by the previously described investigations.

Under ordinary circumstances, however, it is not probable that lime is the dominant base controlling the concentration of phos-

phoric acid in the soil solution, since the great majority of agricultural soils contain vastly more ferric oxide (more or less hydrated) than is equivalent to any amount of phosphoric acid that will ever be brought into the soil; and ferric phosphates are less soluble relatively than lime phosphates. Investigation of the relation of ferric oxide to solutions of phosphoric acid shows that the system is quite similar in many respects to the basic lime phosphates and water just described. When the ratio of iron to phosphoric acid in the solid is greater than that required by the formula of the normal phosphate,  $\text{FePO}_4$ , the aqueous solution will have an acid reaction and contain a mere trace of iron and an amount of phosphoric acid determined by the composition of the solid and by the proportion of solid to water. The basic ferric phosphates seem to be solid solutions which yield a very dilute aqueous solution when brought into contact with water. What the concentration will be under soil conditions is shown by the percolation experiments cited above.

The addition of other substances will in many cases affect more or less the solubility of the soil minerals. If these substances be electrolytes, they will generally, but not always, affect the solubility of the minerals as would be anticipated from the hypothesis of electrolytic dissociation. Thus, the addition of potassium sulphate lessens the solubility and hydrolysis of a potash feldspar or a potash mica. Contrary, however, to the indications of the hypothesis, sodium nitrate decreases the solubility of a ferric phosphate. While appreciable solubility effects take place with sufficiently high concentrations, laboratory experiments indicate that the addition of such substances, even in a liberal application of fertilizers, is not sufficient to produce any great effect on the concentration of the soil solution. Similarly, it has often been supposed that the ammonia, and nitrous and nitric oxides of the atmosphere carried into the soil by rain, or formed in the soil by bacterial action, affect the solubility of the soil minerals, but it is highly improbable that the concentration with respect to these agents ever becomes sufficiently high, as laboratory investigations show to be necessary to affect appreciably the solubility of the ordinary rock- or soil-forming minerals.

Rain brings from the atmosphere into the soil two agents, however, which do markedly affect the solubility of the soil minerals, namely, oxygen and carbon dioxide. The atmosphere within the soil contains normally a somewhat smaller proportion of oxygen than does the air above the soil. Rain in falling through the air absorbs or dissolves relatively more oxygen than nitrogen. Therefore when the rain water has penetrated the soil to any considerable depth there should be, and probably is, a liberation of dissolved oxygen into the atmosphere of the soil interstices. This dissolved oxygen in becoming liberated or when dissolved in the film water appears to be especially active towards the ferrous or ferro-magnesian silicates. These minerals are, moreover, as a class probably the most soluble of the rock-forming silicates. Consequently oxygen brought into the soil in this manner is one of the most important agencies in breaking down and decomposing such minerals as the amphiboles, pyroxenes, chlorites, certain serpentines, phlogopites and biotites; at the same time there is formed ferric oxide (more or less hydrated) and silica (probably as quartz) and magnesium, potassium, calcium or sodium pass into solution, probably as bicarbonates. That the concentration of the soil moisture may thus be made temporarily abnormal is not impossible, though scarcely probable.

The soil atmosphere has normally a decidedly higher content of carbon dioxide than the atmosphere above the soil. Consequently the soil water is always more or less "charged" with carbon dioxide, and the presence of the carbon dioxide decidedly augments the solvent powers of the water towards a great many and different kinds of rock-forming or soil minerals.<sup>1</sup>

What the mechanism of the reaction may be is far from clear.

<sup>1</sup> For references to the literature see Bull. No. 30, Bureau of Soils, U. S. Dept. of Agriculture; also, The action of carbon dioxide under pressure upon a few metal hydroxides at 0° C., by F. K. Cameron and W. O. Robinson, Jour. phys. chem., 12, 561-573, (1908); The influence of colloids and fine suspensions on the solubility of gases in water. Part I. Solubility of carbon dioxide and nitrous oxide, by Alexander Findlay and Henry Jermain Maude Creighton, Trans. Chem. Soc., 97, 536-561, (1910).

The obvious explanation, at least in the case of the ordinary silicates of the alkalis or alkaline earths, is that by forming bicarbonates of the hydrolyzed bases, the active mass of the reaction product with water is decreased and hydrolysis thereby increased. But this explanation is apparently insufficient to account for the effects sometimes observed. It has been shown that the passage of carbon dioxide through solutions of the silicates, will produce more or less slowly a precipitation of silica, and there seems little reason to doubt that it does induce to some degree a decomposition and consequent greater solubility of the silicates of the alkalis and alkaline earths. It also increases to an appreciable extent the solubility of the phosphates of iron, alumina, and lime. Therefore, the variation in the content of carbon dioxide in different soils, and its continual variation from time to time in any one soil, must be expected to produce corresponding changes in the soil solution with respect to such bases as potassium and lime, and also with respect to phosphoric acid. This has been verified experimentally with aqueous extracts of soils, the solutions being charged with carbon dioxide while in contact with the soils.<sup>1</sup> It is not conceivable, however, that any great difference can exist in the partial pressures of carbon dioxide in different soils which are in a condition to support crops, and therefore great absolute differences in the mineral content of the soil solution are not to be anticipated, nor are they actually observed.

It has long been held that the organic substances in the soil have an important solvent effect on the minerals. This assumption seems quite unwarranted in the light of our present knowledge, although it is not to be denied that occasionally there may be present in the soil some soluble organic substance which influences the mineral content. Generally it has been assumed that the effective organic substances influencing the solubility of the minerals are organic acids, of which a number have found their way into past and even current literature, and which have

<sup>1</sup> See, for instance, the results obtained by Peter, Proceedings of the 10th Annual Convention of the Association of American Agricultural Colleges and Experiment Stations, Bull. No. 164, Office of Experiment Stations, U. S. Dept. Agriculture, 1906, p. 151 *et seq.*

been designated as humic, ulmic, crenic, apocrenic, azohumic acids, etc. Their existence has been predicated upon two facts: First, humus is soluble in alkaline solutions but is more or less completely reprecipitated on the addition of an excess of a strong mineral acid, a phenomenon also characteristic of many organic acids. But many other organic substances than acids are also soluble in the presence of alkalis and insoluble in the presence of an excess of strong mineral acids. Second, organic-copper complexes have been obtained from humus constituents, and supposed to be copper salts of various humus acids. The descriptions of these complexes so far given do not show that they met the usual criteria for definite compounds, but indicate on the contrary that they were the results of absorption or possibly adsorption phenomena. Consequently the existence of "humic" acids is purely hypothetical and without experimental or other scientific verification, and calls for no further consideration here.

It is a widespread and popular notion that substances with a slight solubility also dissolve slowly, and that consequently the solubility of the minerals in the soil water must necessarily be a very slow process. This is, however, a misapprehension. It has been shown with a number of the common rock-forming minerals, that if they be powdered and then stirred into a relatively small volume of water, they dissolve very rapidly at first, and in a very short time, generally a few minutes, the solution is nearly saturated with respect to the mineral. Complete saturation, however, may require many days. The general shape of curve expressing the rate of solubility is shown in the accompanying figure.<sup>1</sup> For soils, this fact has been verified repeatedly, in the following way: A cell fitted with parallel electrodes is placed in circuit with a slide-wire<sup>2</sup> or Wheatstone bridge in such a manner that the resistance of the cell contents can be quickly determined. Distilled water is then placed in the cell and its resistance found. Generally this will be up-

<sup>1</sup> See, for example, Umwandlung des Feldspats in Sericit (Kali-glimmer) von Carl Benedick, Bull. Geol. Inst. Upsala, 7, 278-286, (1904).

<sup>2</sup> See Electrical instruments for determining the moisture, temperature and soluble salt content of soils, by L. J. Briggs, Bull. No. 15, and the electric bridge for the determination of soluble salts in soils, by R. O. E. Davis and H. Bryan, Bull. No. 61, Bureau of Soils, U. S. Dept. Agriculture.

wards of 100,000 ohms. The soil or rock powder under examination is then added to the cell, being rapidly stirred into the water contained therein. The resistance drops to about 5,000 ohms within a short space of time, usually three or four minutes. A further slight drop in the resistance generally takes place, *but it requires days, and sometimes even months to become more than barely appreciable.* In this manner it has been

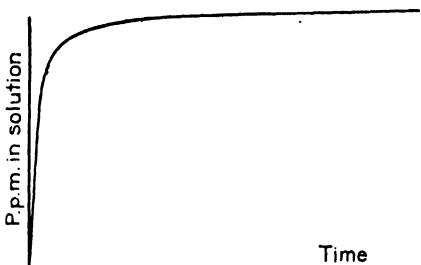


Fig. 3.

shown that the soil and many of the common soil minerals dissolve quite rapidly if they are sufficiently fine to offer a large surface to the action of the water. It would seem to follow, therefore, that in the case of the soil solution the concentration with respect to these constituents derived from the soil minerals, will be rapidly restored whenever disturbed through absorption by plants, leaching, or otherwise.

That the minerals of the soil, or a powdered mineral or rock-powder, will dissolve continually as the concentration of the solution in contact with it is disturbed by abstraction of a dissolved mineral substance, has been shown by numerous experimenters. An apparently obvious way to test this point would be to treat the soil sample with successive portions of water, and to analyze the successive portions for the dissolved mineral substances. This method, however, involves serious experimental difficulties, owing to the smaller sized mineral particles being suspended in the mother liquor, thus precluding satisfactory decantation and clogging filters. Moreover, such a process in no case simulates field conditions. To meet these difficulties, the soil or mineral powder has been placed between two porous

media, as in the space between two concentric cylinders of unglazed porcelain, the space being closed by a rubber stopper. To the interior cylinder is fitted a stopper carrying a tube of insoluble metal, such as platinum or tin. This tube is bent into a goose-neck form, and just below the stopper the tube is perforated with a small opening. The whole apparatus is filled with water and set in a beaker, also filled with water. The metal tube is made the cathode in an electric circuit, a platinum or other suitable anode being introduced into the beaker. In a few minutes the dissolved and hydrolyzed bases pass into the cathode chamber, and as the water also accumulates in the chamber by electrolytic endosmosis, a solution of the bases dissolved from the soil minerals drops from the end of the metal goose-neck. By adding water to the outer beaker from time to time, a steady stream of alkaline solution has been obtained for months, and in no case yet has a soil thus treated failed to continue to yield up the bases it contains in its mineral particles. The acids, such as phosphoric acid for example, are of course found in the water outside the porous cells, and in the case of the phosphoric acid it also appears to continue indefinitely to be withdrawn from the soil.<sup>1</sup> It thus appears that as the products of solution and hydrolysis are removed, by such an endosmotic device as that just described or by the roots of growing plants, by leaching or otherwise, the soil minerals will continue to dissolve.

The foregoing arguments as to the concentration of the soil solution with respect to those constituents derived from the soil minerals, are based on the generally recognized principle that a material system left to itself tends towards a condition of stable equilibrium or final rest, that is, a condition where such changes as are taking place are so balanced that no change occurs in the system as a whole. But the soil is a system continually subject to outside forces and influences, and as pointed out above, is of necessity a dynamic system. It is doubtful in the extreme if any soil in place is ever in a state of final stable equilibrium. It would be natural, therefore, to expect and to

<sup>1</sup> For detailed description of the apparatus and experimental data, see Bull. No. 30, p. 27, *et seq.*, Bureau of Soils, U. S. Dept. Agriculture.

find that even if the solution in the soil were dependent on the solubility of the soil minerals alone and were continually tending towards a definite normal concentration, actually this concentration would seldom if ever be realized. Most important in this connection is the fact that the concentration of the soil solution is always dependent in some degree upon the concentration of the soluble constituents in the solid phases in other than definite chemical combinations. Other factors affecting the concentration of the mineral constituents in the soil solution are always existent, and theoretically at least, can not be ignored. Nevertheless *a priori* reasoning as well as the experimental evidence at hand indicates that the various processes taking place in the soil as a whole continually tend to form and maintain a normal concentration of mineral constituents in the soil solution.

## Chapter VIII.

### ABSORPTION BY SOILS.

A property of soils, affecting profoundly the composition and concentration of the soil solution, is absorption.<sup>1</sup> It is generally recognized that soils are good absorbers for vapors, and this fact finds practical expression in the common practice of burying things with a disagreeable odor, such as animal carcasses, night-soil, etc. It is also well-known that dissolved as well as suspended material can be more or less completely removed from water by passing it through sand or soil, and this fact finds important application in water supplies for cities and towns, sewage disposal, etc. It was known as long ago as Aristotle's time that ordinary salt is partly removed from water by passing through sand or soil. In recent times the practical as well as theoretical importance of this phenomenon has led to considerable study and experimental research, so that our knowledge of absorption effects is now fairly extensive, though it can hardly be claimed that it is satisfactory. The absorption of a dissolved substance from solution by a soil may be one or more of at least three kinds of phenomena. It may be a mechanical inclusion or trapping, distinguished by the term *imbibition*, the most familiar and striking case being the absorption of water itself by soil or sponge or similar medium. It may be a partial taking up of the dissolved substance to form a new compound or a *solid solution*,<sup>2</sup> as probably is the absorption of phosphoric acid by

<sup>1</sup> For a detailed discussion and citations of the literature, see: Absorption of vapors and gases by soils, by H. E. Patten and F. E. Gallagher, Bull. No. 51; and Absorption by soils, by H. E. Patten and W. H. Wagggaman, Bull. No. 52, Bureau of Soils, U. S. Dept. Agriculture, 1908.

<sup>2</sup> That is, a homogeneous solid, which may be either crystalline or amorphous. Probably the readiest criterion for distinguishing between a definite compound and a solid solution, is that the former is stable in contact with a liquid solution of its constituents over a measurable range of concentrations, while the composition of the solid solution changes with every change in the concentration of the liquid solution in contact with it.

lime or ferric oxide. Or it may be a condensation or concentration of the dissolved substance on or about the surface of the absorbing medium, a phenomenon known as *adsorption*. To prove the existence of adsorption definitely and conclusively in any given case is always difficult, if ever possible, but the existence of this phenomenon is the most logical explanation of many observations, and is generally admitted by chemists and physicists at the present time.<sup>1</sup> It is by adsorption, probably, that potash and ammonia are held by the soil when added in fertilizers.

That absorption is dependent in some manner upon the solubility of the dissolved substance in the particular solvent employed would seem to be obvious. But what the relation may be, if it exists at all, is not known. For instance, silk absorbs picric acid from solutions in water and alcohol but not from solutions in benzene, although the solubility of picric acid in benzene lies between its solubility in water and in alcohol.<sup>2</sup>

The absorption of any given dissolved substance from different solvents is markedly different. Most soils absorb methylene blue from aqueous solutions with great avidity, but washing out the absorbed dye with water is an extremely tedious and unsatisfactory process, although the dye can be readily and more or less completely removed from the soil by alcohol. As might be anticipated from this, it is known that the presence of one dissolved substance affects the absorption of another, but in what way can not, generally, be anticipated, although it would seem that the importance of this subject for manurial practice would invite further research.

From the same solution, different absorbents remove a dis-

<sup>1</sup> A clear and apparently indisputable case of adsorption has been noted by Patten (*Some surface factors affecting distribution*, Trans. Am. Electrochem. Soc., 10, 67-74, 1906). On adding powdered quartz to an aqueous solution of gentian violet, there is a distribution of the dye between the water and the quartz. A microscopic examination of the latter showed that the dye was concentrated in thin layers upon the surface of the quartz grains, from which it could be washed with water, no change in the quartz grains being noticeable.

<sup>2</sup> Absorption of dilute acids by silk, by James Walker and James R. Appleyard, Jour. Chem. Soc., 69, 1334-1349, (1896).

solved substance in different degrees. Speaking generally, paper absorbs dyes more readily than do soils, while soils absorb bases more readily than does paper. Hence the reddening of litmus paper when in contact with a moist soil. Heavy soils or soils containing much hydrated ferric oxide absorb bases more readily than do light soils, but this is probably owing to relative amounts of surface exposed, for the same relation holds true with respect to phosphoric acid. Soils rich in humus are better absorbers than soils not so rich. But here again there is yet doubt as to whether the explanation lies in the amount or in the kind of surface acting.

From the same solvent different dissolved substances are absorbed quite differently by any given absorbent. This can be readily illustrated again by dyes. If an aqueous solution of a mixture of methylene blue and sodium eosine, for instance, be shaken up with a soil, or percolated through a column of soil, the methylene blue is absorbed the more quickly and completely and a partial separation of the two dyes can be readily effected, the separation being more or less complete according to the conditions of the experiment. In the same manner two salts in solution can be separated partially at least.<sup>1</sup> Soils absorb potassium more readily than sodium; magnesium more readily than lime; and ammonia more readily than any of these bases.<sup>2</sup>

The absorption from aqueous solutions of inorganic salts involves a most interesting complication. Just as a mixture of two or more dyes or salts in solution can be separated by the selective action of an absorbent, so can an electrolyte itself be decomposed or resolved. Thus, if a solution of potassium

<sup>1</sup>For a number of interesting examples, see, Ueber das Aufsteigen von Salzlösungen in Filtrirpapier, von Emil Fischer und Edward Schmidmer, Liebig's Annalen der Chemie, 272, 156-160, (1893).

<sup>2</sup>The prompt absorption of a base by soils is shown by the following experiment: To some freshly boiled distilled water add several drops of alcoholic phenolphthalein, and then just enough base to produce a decided red color. If the solution be now passed through a short column of soil, cotton, shredded filter-paper or similar absorbent, the percolate will be perfectly colorless. The red color will be restored, however, by adding a little of the base to the percolate.

chloride be passed through a column of soil, or cotton, or paper, or any similar absorbent, the filtrate will not only be less concentrated than the original solution, but the potassium will be found to have been absorbed to a greater extent than the chlorine, that is, the percolate contains free hydrochloric acid. The importance of this phenomenon for the conservation of the desirable constituents of manurial salts, and the elimination or leaching out of the less desirable constituents is obviously great. Equally great perhaps, is the effect upon the reaction of the soil, whether it be rendered temporarily alkaline or acid, an effect of the very greatest importance for the growth of some of our common crop plants<sup>1</sup> and for the lower soil organisms, such as the bacteria, molds, together with fermenters, enzymes, etc., many of which are very sensitive to the reaction of the media in which they may be, and which in turn are of undoubted importance in determining the fertility of the soil for higher plants.

The absorption of a dissolved substance from solution by an absorbent is in effect a distribution phenomenon and the simplest formula to give quantitative expression to such a distribution is  $C/C^1 = K$  when C is the concentration in the liquid phase and  $C^1$  the concentration in the solid phase, K being a characteristic constant for the particular case under consideration. When a chemical reaction or a change of state, chemical or physical, is involved in the absorption in either dissolved substance or absorbent the formula becomes  $C^n/C^1 = K$  when n is a function which may be very simple or very complex. Attempts to develop a precise formula of this general type for the absorption by some given soil, although such a formula would be desirable for

<sup>1</sup> See, The toxic action of acids and salts on seedlings, by F. K. Cameron and J. F. Breazeale, Jour. Phys. Chem., 8, 1-13, (1904). It is quite conceivable, for instance, that if the drainage conditions were not exceptionally good under a heavy type of soil, it might be rendered temporarily unfit for clover or alfalfa by a heavy application of potassium salts or of sodium nitrate. The idea put forward by some authorities that too long continued or over fertilizing renders soils acid, may have better foundation than their theoretical reasoning would seem to warrant.

theoretical and practical reasons alike, have uniformly failed. A sufficient reason for this failure seems to lie in the fact that most dissolved substances produce an appreciable effect on the granulation or flocculation of the soil particles, which is progressive with the absorption so that a continual change of absorbing or effective surface is taking place as the absorption proceeds.<sup>1</sup> Moreover, in the case of an absorption, with the formation of a continuous film of the dissolved substance, a new kind of absorbing surface is developed. Hence  $n$  is a function of so difficult a character as to defy thus far any attempt at formulation.<sup>2</sup>

We cannot therefore predict in any quantitative way what will be the distribution of a soluble substance such as salts in commercial fertilizers, for instance, between the solid soil particles and the soil solution. Empirical experiments show, however, that with the amount of a soluble salt present under normal conditions in a humid climate, or as used in fertilizer practice, the absorption of ammonia, lime, potassium or phosphoric acid is relatively very great, and in a general way in about the order named.

Absorption is not an instantaneous process. However, the rate at which a dissolved substance is absorbed is generally quite rapid. That is, if a soil be stirred or mixed with an aqueous

<sup>1</sup> That mineral fertilizers have a decided influence on the granulation of soils and the properties dependent thereon, and that this is of practical importance, is gradually coming to be recognized; see, for instance, Ein Beitrag zur Kenntnis der Wirkung künstlicher Dünger auf die Durchlässigkeit des Bodens für Wasser, von Edwin Blanck, Landw. Jahrb., 38, 863-869, (1909), and the literature there cited. Dr. R. O. E. Davis in a yet unpublished investigation has shown that the addition of soluble salts produces decided effects upon the soil-moisture relations which affect crop production. The critical moisture content is displaced, the penetrability, permeability, specific volume, vapor tension, etc., are affected in measurable degree, and it appears that the physical functions of mineral fertilizers are much greater in amount and importance than has been popularly assumed.

<sup>2</sup> The distribution of solute between water and soil, by F. K. Cameron and H. E. Patten, Jour. Phys. Chem., 11, 581-593, (1907).

solution, the absorption takes place very quickly, in the absence of any outside disturbing influences. The law governing the rate of absorption by soils has not therefore possessed any great practical interest and has not been studied from a quantitative point of view, although it is known qualitatively that the rate is increased by increasing the concentration of the solution, or by increasing the amount of the absorbent or at least its effective surface. Two rate equations are of interest in this connection, and have been carefully studied. The rate at which a salt or other dissolved substance will advance into an absorbing soil from a solution is given by the same equation as that describing the rate of advance of the water itself,  $y^n = kt$  where  $y$  is the distance and  $t$  the time.<sup>1</sup> The constants  $n$  and  $k$  for the slower moving dissolved substance are different from those for the water. This equation has probably little importance for ordinary agriculture, for absorption by the soil from a large (and relatively immeasurable) mass of solution is unusual. That it may have considerable importance in seepage, irrigation, and some soil engineering problems, seems quite likely.

The rate at which a soil will absorb a dissolved substance from a percolating solution is given by the equation  $dx/dt = K(A - x)$ , as has been pointed out above.<sup>2</sup> More interesting and important, however, is the fact that this same equation describes the rate at which an absorbed substance is removed from the soil by leaching. In the case of soils in humid areas  $dx/dt$  rapidly becomes exceedingly small as  $x$  approaches  $A$ , that is, when the amount of soluble material in the soil becomes small, and is practically constant under such conditions, as has been pointed out above when describing the removal of potassium and phosphoric acid from soils by percolating waters. This formula has a special interest in considering the reclamation of alkali lands by underdrainage, a problem to which reference will be made later.

Both percolation experiments, as those cited above, and direct absorption experiments made by shaking up soils with solutions

<sup>1</sup> See formula, page 28.

<sup>2</sup> See formula, page 47.

of the salts in question, show conclusively that the absorption phenomena taking place in the soil are in harmony with the direct solubility effects in tending to produce and maintain a solution of a normal concentration as regards those constituents which it happens are also derived from the soil minerals.<sup>1</sup> It is an interesting coincidence that nitric acid (in combination with various bases of course) is very little absorbed by most soils, and does vary in concentration, not only in different soils but in the same soil, between wide limits, and within short intervals of time.<sup>2</sup> The nitrates of the soil are not derived from minerals, and should more properly be considered with the organic constituents of the soil solution.

An important application of these views concerning absorption arises in connection with certain widespread notions concerning soil acidity. There is a popular belief that most soils are acid, that the soil solution contains some free acid, mineral or organic, other than dissolved carbon dioxide, and that a neutral or alkaline solution is necessary to the successful production of most of our crops. This belief is, however, unwarranted, for the vast majority of soils yield an aqueous extract which is alkaline when boiled to expel carbon dioxide, and some of our crops, for instance wheat, seem to thrive better in a slightly acid medium. This popular fallacy seems to have its

<sup>1</sup> An extreme case is worth citing in this connection. Mr. W. H. Heileman in studying the influence of various kinds of alkali upon plant growth, added from 3-4 per cent. of sodium carbonate to soils known to be otherwise free from alkali. Wheat seedlings grown in the soils so treated showed no ill effects from the added salt. When distilled water was percolated slowly through the soils, or shaken up with them, the resulting solution contained the merest traces of the alkali.

The ordinary method of determining the lime requirement of a soil by adding lime water until the solution shows an alkaline reaction, is another obvious absorption phenomenon, and is not dependent, as popularly supposed, upon the presence of acids in the soil. Soils which by no possibility could contain any free acid, frequently absorb very large amounts of lime in this manner.

<sup>2</sup> Usually, in the growing season, the soil solution has a much higher concentration with respect to nitrates in the morning than it has in the evening.

origin in the fact that most soils when moistened and pressed against blue litmus paper, redden it. This reddening may sometimes be due to the actual presence of some acid, or to dissolved carbon dioxide, but is undoubtedly due in the majority of cases to selective absorption. Litmus is a red dye of an acid-like character, which forms a soluble blue salt with the ordinary bases. But it has been shown that most soils are better absorbents of bases than is paper, whereas paper is a better absorbent of dye, speaking generally, than is a soil. Consequently when moist soil is brought into contact with wetted blue litmus paper the base is absorbed more readily by the soil, and the dye by the paper, the latter therefore becoming reddened.

The reddening of blue or "neutral" litmus paper can be accomplished with various absorbents. By pressing the litmus paper between moistened wads of absorbent cotton the reddening can be readily accomplished, usually in the course of ten minutes to a half hour. That the phenomenon is not due to any adhering acid on the cotton can be shown in the following way: A litmus solution is carefully prepared so that there is a very small excess of base present over that required to give the blue color. A wad of absorbent cotton is carefully washed by repeatedly sousing it in distilled water from which carbon dioxide has been expelled by boiling. When the cotton has been thoroughly washed, it is stirred thoroughly in a portion of distilled water, free from carbon dioxide, then withdrawn by some appropriate instrument and allowed to drain for a few minutes. The litmus is added in fairly large quantity to the drainings, which should then have a blue color. Again stir the cotton in the water, and more or less quickly, depending on the amount and purity of the litmus preparation as well as the quantity of cotton used, the solution will become red. The only criterion for determining surely that a soil is acid, is to make an aqueous extract, expel the dissolved carbon dioxide by boiling, or by passing through the solution an inactive gas, such as nitrogen, and then to test the reaction of the solution. Acid soils undoubtedly do exist, but they are by no means common or widespread, and are to be regarded as exceptional and abnormal.

The phenomena of selective absorption suggest the important part which surfaces play in modifying and changing chemical reactions.<sup>1</sup> For instance, Becquerel<sup>2</sup> observed that a solution of copper nitrate or cobalt chloride diffusing from a cracked test-tube placed in a solution of sodium sulphide, led to the formation of the corresponding sulphide, but in the crack the metal itself was precipitated. Experiments of Graham<sup>3</sup> show that when a solution of silver nitrate is percolated through charcoal, not only is there a selective absorption as is shown by the percolate containing free acid, but there is a chemical reaction involved, since the silver is deposited in metallic spangles in the interstices of the absorbent. Graham has shown, and since his time others, that often metals can be separated from solutions of their salts by such absorbents as charcoal. Spring<sup>4</sup> has shown that at bounding surfaces of dilute solutions, chemical action is increased.

It has been shown that the amount and kind of surface has a marked influence on the decomposition of hypochlorous acid, carbon dioxide, phosphine, arsine, and other compounds. Meyer and his associates, as well as a number of other investigators, have shown that the character of the surface of the containing vessel greatly affects the combination of hydrogen and oxygen. Many reactions have been investigated by van't Hoff, who concludes that both the nature and amount of surface exposed have an influence. The inversion of sugar is affected by the nature of the walls of the containing vessel, and its reduction by Fehling's solution is affected both by the walls of the vessel and the amount of cuprous oxide formed in the reaction. Alteration in the character as well as degree of a number of reactions by having them take place in capillary spaces has been observed

<sup>1</sup> For references to the literature see, Bull. No. 30, Bureau of Soils, U. S. Dept. Agriculture, p. 61 *et seq.*

<sup>2</sup> Note sur les réductions métalliques produites dans les espaces capillaires, par M. Becquerel, Comptes rendus, 82, 354-356, (1876).

<sup>3</sup> Effects of animal charcoal on solutions, by T. Graham, Quart. Jour. Sci., 1, 120-125, (1830).

<sup>4</sup> Über eine Zunahme chemischer Energie an der freien Oberfläche flüssiger Körper, von W. Spring, Zeit. physik. Chem., 4, 658-662, (1889).

by Liebreich, Becquerel, Lieving and other investigators. So-called "contact reactions," as in the production of sulphuric acid, are now familiar processes finding commercial applications. And the solubility of some substances at least, notably gypsum, has been shown to vary considerably with the size and consequent shape of the particles in the solid substance in contact with its solution.<sup>1</sup>

It has been shown that some soils will at times produce the blue coloration in alcoholic solutions of guiac, which is characteristic of oxidases, and yellow aloin solutions are sometimes colored red. Hydrogen peroxide is decomposed by some soils even after they have been thoroughly ignited to get rid of all organic matter. But in how far these effects may be due to surface influences can not be positively stated; yet uncompleted investigations by Dr. M. X. Sullivan indicate that some of these phenomena at least must be attributed to specific influences (although probably of catalytic character) of particular soil components, such possibly as manganous oxide or ferric oxide; but the mechanism of the reactions is as yet largely speculative.

The soil is composed in large part of very fine particles of rounded shape, exposing relatively an enormous surface to the soil solution, and normally this solution is mainly under capillary conditions, so that we should expect that many reactions would take place quite differently in the soil from the way they would in a beaker or flask. This fact has been generally overlooked or ignored, and is probably the explanation of many of the apparently anomalous results hitherto reported in chemical investigations of soils. Abnormal solubilities, precipitations, oxidations or reductions are frequently found in the literature, and when their abnormality is noted at all, they are too often and with slight show of reason ascribed to indefinite bacterial action or more mysterious vital agencies. Many of them are undoubtedly the results of surface actions. Unfortunately, aside from

<sup>1</sup> See especially, Beziehungen zwischen Oberflächenspannung und Löslichkeit, von G. A. Hulett, Zeit. Phys. Chem., **37** 385-406, (1901). Löslichkeit und Löslichkeits Beeinflussung, von V. Rothmund, p. 109, (1907); Principles théoretiques des méthodes d'analyse minérale, par G. Chesneau, p. 16-25, (1906).

some few studies of absorption phenomena, surface effects have received little or no attention from soil investigators, although obviously one of the most important and apparently fruitful fields, requiring immediate attention. Enough is known to justify the statement that the chemistry of the soil need not be, and probably is not, the chemistry of the beaker.

## Chapter IX.

### THE RELATION OF PLANT GROWTH TO CONCENTRATION.

That the concentration of the mineral constituents in the soil solution under normal conditions is competent for plant support, is shown by numerous experiments. Birner and Lucanus<sup>1</sup> in an experiment that has long since become classic, found that they could raise wheat to maturity in a well-water, the concentration of which was approximately 18 parts per million with respect to potassium, and 2 parts per million with respect to phosphoric acid, while the corresponding concentrations of the soil solution are normally about 25-30 parts per million of potassium and 6-8 parts per million of phosphoric acid. Nevertheless Birner and Lucanus report that the wheat grown in the well-water thrived even better than that grown at the same time in a rich garden mold. Since then many investigators in numerous trials have obtained similar results. Recently wheat, corn, and some of the common grasses have been grown to a satisfactory maturity in tap water, with a concentration of about 7 parts per million of potassium and 0.5 parts per million of phosphoric acid. And repeatedly wheat plants, grasses, cowpeas, vetches, potatoes and other plants have grown in a satisfactory way in solutions made by shaking up a soil in distilled water and separating from the solid particles by means of filters of unglazed porcelain.

There can be no doubt, therefore, that the soil solution is normally of a concentration amply sufficient to support ordinary crop plants, and is maintained at a sufficient concentration, so far as mineral plant nutrients are concerned. Undoubtedly, however, variations in the concentration of the soil solution can, and often do, take place, and the results of laboratory experiment indicate that they probably produce effects on plants.

It has been shown in water-culture experiments with wheat, that if a given ratio of mineral nutrients be maintained, relatively small effect is produced on the growing plants by varying the

<sup>1</sup> Wasserculturversuche mit Hafer, von Dr. Birner und Dr. Lucanus, Landw. Vers.-Sta., 8, 128-177, (1866).

concentration over a wide range, in one case from 75 parts per million to 750 parts per million,<sup>1</sup> and this effect seems to be largely independent of the nature of the particular mixture of solutes. But varying the relative proportions of the mineral constituents has been shown by numerous experiments to produce very marked changes in the growth of plants. Not only does a control of the concentration and proportion of the mineral constituents of a solution produce a more rapid, or a slower growth, a greater or lesser total growth, but it produces differences in the character of growth; as for instance, causing the tops to grow relatively faster than the roots, or *vice versa*. However, many effects of this type can be produced, and sometimes more readily, by soluble organic substances, or mechanical agencies. The mechanism of these effects is by no means clear, in many cases. That other causes obtain than a sufficient supply of mineral nutrients will be shown in the following chapters. Experiments with wheat seedlings in water cultures, where the weights of the green tops were taken as the measure of growth, showed that the most favorable ratio was one of phosphoric acid ( $\text{PO}_4$ ) to three or four of potassium (K), about the ratio which has been found to exist normally in the soil solution of humid areas of the United States, namely, 6.8 parts per million of phosphoric acid to 25-30 parts per million of potassium.

All growing plants require for their growth and development various organic compounds containing carbon, hydrogen, oxygen and nitrogen. The higher crop plants with which agricultural investigations appear to be more immediately concerned, seem to have inherent power to produce these needed substances within themselves. But it is becoming more and more evident that the large problem of soil fertility, or the relation of the soil to crop production, frequently if not generally involves the growth and development of lower organisms including ferment and bacteria. These may or may not in particular cases, favor the growth of the desired higher plants. Many of these lower organisms require certain organic compounds or thrive better

<sup>1</sup>Effect of the concentration of the nutrient solution upon wheat cultures, by J. F. Breazeale, Science, n. s., 22, 146-149. (1905).

if these are brought to them in the soil solution, and indeed evidence is not lacking that such may sometimes be the case even with the higher plants. Certainly their growth can be much affected by the presence of different organic substances in the nutrient solution. Enough work has been done in this field of investigation to show that the concentration of the soil solution or artificial nutrient solution with respect to the organic compounds must generally be low; too high a concentration always inhibits growth or even produces death; and there is probably an optimum concentration, or one at which the plant will grow best; but this optimum concentration varies with the specific nature of the plant, the presence of other dissolved substances, mineral or organic, and possibly with other factors. While a notable amount of work has thus been done in a field of inquiry obviously of practical as well as theoretical interest, almost no definite information has as yet been obtained as to the concentration of organic substances in the soil solution, or its effect upon plants under field conditions, excepting in the case of the nitrates, the products of bacterial activities. The concentration with respect to nitrates is known to vary greatly from a few parts to several thousand parts per million, and this sometimes within a few days or even hours. The great changes in concentration with respect to nitrates, the rapidity of the changes, and the correspondingly large effects on growing plants make this a subject requiring special treatment by itself. This at present seems more easily appreciated from a consideration of the bacteria involved, and will not be discussed more fully here.<sup>1</sup>

Of the ash constituents of plants, there must be in the soil solution, potassium, magnesium, phosphorus, sulphur and iron for any plant growth, and for the higher crop plants, calcium

<sup>1</sup> See: The fixation of atmospheric nitrogen by bacteria, by J. G. Lipman, Bull. No. 81, Bureau of Chemistry, U. S. Dept. of Agriculture, 1904; A review of investigations in soil bacteriology, by Edward B. Voorhees and Jacob G. Lipman, Bull. No. 194, Office of Experiment Stations, U. S. Dept. of Agriculture, 1907; The physiology of plants, by W. Pfeffer, translated by A. J. Ewart, vol. 1, p. 388 *et seq.*, 1900; The effect of partial sterilization of soil on the production of plant food, by Edward John Russell and Henry Brougham Hutchinson, *Jour. Agric. Sci.*, 3, 111-144, (1909).

must also be present. Of these, iron is usually present in barely appreciable concentration and more than this is not desirable, or is even harmful for common crop plants. Under the normal conditions for soils in humid areas, sulphur also is usually present in scarcely more than appreciable quantities and there is no positive evidence to show that higher concentrations are especially desirable, though this may be the case for certain crops, such for instance as the onion. Phosphorus is usually present to the extent of 5 or 6 parts per million of phosphoric acid ( $P_2O_5$ ), while it has repeatedly been shown that such crops as wheat can thrive and make a good growth with a concentration a tenth of this. It appears to be clear therefore that as far as food supply is concerned there is normally an ample supply of phosphorus in the soil solution; but it does not follow that increasing the concentration of the solution if only temporarily would not result in favorable effects upon growing plants.

A consideration of the bases, however, introduces serious difficulties, which will probably require much further research by the plant physiologist as well as the soil chemist. It is impossible as yet to determine the concentrations at which different plants will not grow. It is even impossible to determine the concentrations at which they will thrive best. It seems certain that different crop plants require different amounts of these minerals, but whether or not they require different concentrations of the constituents in the nutrient solution for their several best growths is yet not clearly shown. It now seems probable that to some extent at least these basic mineral nutrients can replace one another for the plant's metabolism. It has been shown in the case of certain lower plant organisms that potassium can be more or less successfully replaced by rubidium and caesium, and in the case of some higher plants, possibly calcium, magnesium and potassium can partially replace one another.<sup>1</sup> In spite of the fact that sodium as well as potassium is a necessary constituent for the metabolism of higher animals which feed upon

<sup>1</sup> For a more detailed discussion of this subject, and the functions of the several ash constituents in plant nutrition, see: *The physiology of plants*, by W. Pfeffer, translated by A. J. Ewart, vol. 1, p. 410, *et seq.*, 1900.

plants, it is generally held that sodium can not replace potassium in the processes of plant growth, although Wheeler and his colleagues have advanced evidence to show that a partial replacement is possible.<sup>1</sup> It seems evident, however, that no generalizations can hold concerning the effect of the concentration of any one base on plant growth which do not include recognition of possible modifications due to the presence of other bases; and the formulation of such generalizations must needs wait upon a more thorough knowledge of the parts played by the several mineral nutrients in the metabolism of different classes of plants.

As to forms or chemical combinations in which the inorganic constituents of the soil solution are best adapted to plant growth, but little can yet be said other than that the different combinations do have an importance. Some empirical information is available, such as for instance, that potassium sulphate or carbonate is a better fertilizer for some crops than is potassium chloride. It is known that the mineral nutrients in the plant are partly in inorganic combinations but largely in organic combinations. But the causal relationships are yet to be worked out. And finally, although some meagre experimental data have been obtained as to the effect of certain inorganic constituents on the absorption of others, by particular plants, the mechanism of absorption itself, including the selective powers of the plant, is yet wanting an adequate explanation.

<sup>1</sup> The effect of the addition of sodium to deficient amounts of potassium, upon the growth of plants in both water and sand culture, by B. L. Hartwell, H. J. Wheeler and F. R. Pember, Report Rhode Island Agricultural Experiment Station, 1906-7, p. 299-357.

## Chapter X.

### THE BALANCE BETWEEN SUPPLY AND REMOVAL OF MINERAL PLANT NUTRIENTS.

The mechanism of the solution and transport of mineral nutrients developed in the preceding pages makes it of interest to determine the relation between the possible or probable supply of mineral plant nutrients and crop demands over large areas. The inquiry can be formulated more specifically: Is the movement of mineral plant nutrients towards the surface soil equal to or in excess of the removal by drainage waters and garnered crops? Satisfactory data are yet wanting for anything like exact computations, but approximate figures are available which appear sufficient for the present purpose.

The rainfall ( $R$ ) can be considered as disposed in three portions, the fly-off ( $f$ ), the run-off ( $r$ ), and the cut-off ( $c$ ). Stating this as an equation,

$$R = f + r + c.$$

The cut-off can be resolved into the portion ( $a$ ) seeping through the soil to ultimately join the run-off, and the portion ( $b$ ) returning to the surface to ultimately join the fly-off. Stated as equations,

$$\begin{aligned} R &= f + r + a + b \\ &= f + b + (r + a). \end{aligned}$$

In other words, the rainfall can also be considered as made up of the fly-off, the capillary water of the soil and the drainage from the area. According to Murray,<sup>1</sup> Geikie,<sup>2</sup> Newell,<sup>3</sup> and others, the drainage water for humid areas, or such an area as the United States as a whole, would be between 20 and 30 per cent. of the rainfall, the major portion coming from seepage water rather than surface drainage. Assuming the higher fig-

<sup>1</sup> On the total annual rainfall on the land of the globe, and the relation of rainfall to the annual discharge of rivers, by Sir John Murray, Scot. Geog. Mag., 3, 65-77, (1887).

<sup>2</sup> Textbook of Geology, by Sir Archibald Geikie, p. 484, (1903).

<sup>3</sup> In Principles and conditions of the movements of ground water, by F. H. King, Ann. rept. U. S. Geol. Surv., 19, II, 59-294, (1897-98).

ure, and making the further very probable assumption that the capillary water in the soil (*b*) is never less than the fly-off or the water that evaporates during rain (*f*), it follows from the equations given that the capillary water is at least 35 per cent. of the rainfall. If we assume the lower value for the drainage, then the capillary water is at least 40 per cent. of the rainfall, and if we assume the extreme case—that the fly-off is practically negligible—the capillary water becomes 80 per cent. of the rainfall. It appears, therefore, that in all probability the proportion of the cut-off water which returns to the surface as film water or capillary water is always greater, and generally much greater, than the portion which seeps through the soil to join the run-off.

From the available data, it appears that the average concentration of the run-off waters of the United States is about 1.8 parts per million of potassium (K) and about 0.6 parts per million of phosphoric acid ( $\text{PO}_4$ ),<sup>1</sup> while the concentration of the capillary groundwater is some ten or twelve times greater. But even if these concentrations were the same, it is altogether probable that very much the greater part of the mineral plant nutrients dissolved by meteoric waters is continually, if slowly, moving towards the surface of the soil.

The average rainfall of the United States may be taken as approximately 30 inches.<sup>2</sup> If it be assumed that the discharge into the sea is 25 per cent., then the capillary cut-off water is at least 37.5, and probably nearer 70 per cent. of the rainfall. King's experimental work<sup>3</sup> indicates that the higher figure is much nearer the truth. Computing from the concentrations just cited, with the equations given above, it is found that approximately 3,500,000 tons of potassium (K) and 1,200,000 tons

<sup>1</sup> Estimated from data in Bull. No. 330, U. S. Geological Survey, The data of geochemistry, by Frank Wigglesworth Clarke, 1908, p. 53-90.

<sup>2</sup> The latest authoritative statement is that the average annual rainfall of the United States is 29.4 inches; see: Water Resources, by W J McGee, vol. 1, p. 39-49, and Distribution of rainfall, by Henry Gannett, vol. 2, p. 10-12, Report of the National conservation commission, Senate doc. No. 676, 60th Congress, 2d session, 1909.

<sup>3</sup> King: loc. cit., p. 85.

of phosphoric acid ( $\text{PO}_4$ ) are carried into the sea annually from the United States, while from 48,000,000 to 100,000,000 tons of potassium and 18,000,000 to 40,000,000 tons of phosphoric acid are being carried towards the surface of the soil. If it be assumed that an average of one ton per acre of dry crop containing one per cent. potash and 0.6 per cent. phosphoric acid<sup>1</sup> be removed from the entire area of the United States, then the annual loss from this source would be 24,000,000 tons of potassium and 14,000,000 tons of phosphoric acid. Consequently, there is an ample margin between the losses by cropping and seepage waters, and the supply of capillary waters. It is true that cases exist where the production of vegetable matter is much greater than a ton to the acre, productions of five tons or even more being on record. But such cases occur only where the water supply is also greater, either through natural rainfall or artificial irrigation; and it should also be borne in mind that the production of so large a mass of green crop involves a considerable drawing power on the water in the soil in addition to the evaporation which would take place at the surface under ordinary conditions. In other words, the plant would then be playing no small part in drawing to itself its needed supplies of water and dissolved mineral nutrients.

The question may be asked, if the processes outlined above are generally operative, why accumulations of soluble mineral substances are not usually found at the surface of the soil. As a matter of fact such accumulations do occur normally when the evaporation at the surface is relatively large, that is, under arid conditions. And under humid conditions it appears to be a general rule that the surface soil contains more readily soluble or absorbed mineral matter than do sub-soils.<sup>2</sup> No great accumula-

<sup>1</sup> Estimated from Wolff's tables, *How crops grow*, by Samuel W. Johnson, 1890, appendix.

<sup>2</sup> See, for instance: *Investigations in soil management*, by F. H. King, Madison, Wis., 1904, p. 62 *et seq.* This tendency towards a higher content of absorbed soluble mineral matter in the surface soil has been amply confirmed by other experiments. It has been advanced as an argument against the assumption that the hydrolysis of the soil minerals is a reversible process. But as pointed out elsewhere in the text, many of the soil minerals can be made in the wet way at more or less elevated temperatures and the more rational explanation is simply that at ordinary temperatures the rate of formation is exceedingly slow.

tion occurs at the surface normally under humid conditions because the rainfall is sufficiently distributed throughout the year to enable the cut-off water to carry back promptly into the lower soil levels any excessive amount of soluble material, there to start anew its slower ascent towards the surface.

Calculations such as those here presented are at the best open to many objections, and it is wise to avoid giving them too much emphasis. So far as the available data justify any conclusion, however, it appears that the rise of capillary water is entirely capable of maintaining a sufficient supply of mineral nutrients for crop requirements; and furthermore, it is obvious that the problem of the supply of mineral plant nutrients is dynamic and cannot be successfully attacked by considerations which are essentially static.

## **Chapter XI.**

### **THE ORGANIC CONSTITUENTS OF THE SOIL SOLUTION.**

The organic substances in the soil are tissue remains, to a large extent of plants, and to a less extent of animals; and it is to be expected that there may be found also in the soil the substances which were in the organisms at the time of their death, and degradation and decomposition products derived from these. Moreover, there are to be anticipated numerous products of bacterial origin, secretions of algae, fungi, etc., so that the organic complex in the soil may contain numerous substances of widely different chemical characteristics. Degradation products of proteins, fats, and carbohydrates, as well as decomposition products may be expected in almost any soil. But it does not follow that any particular organic substance (excluding, of course, carbon dioxide or nitrates) is to be found in every soil. No generalization regarding the organic substances in the soil can be made such as that formulated for the inorganic compounds. It is probable that further investigation will show certain organic substances or classes of substances to be common to most soils, but it is reasonably certain that many other organic substances will be found in only a few soils, or occasionally, and these latter will be often a prominent factor characterizing the particular soil in which they may occur.

Although no broad generalization is justified regarding the composition of the soil solution with respect to organic substances dissolved, nevertheless the extension of the methods developed in the study of the inorganic substances dissolved has led to a considerable knowledge of the organic ones.

In view of the facts shown in the preceding chapters, and at the same time recognizing that good and poor soils respectively must show differences in the soil solution if the fundamental thesis is valid as to the relation of soils to crop production, experiments have been made to investigate in a comparative way solutions obtained from good and poor soils of the same type, locality, and physical characteristics. For this purpose two samples of soil were taken from adjacent fields which had

been under observation for two years. The soils were of the same type, Cecil clay, and were so similar in their physical characteristics as to be distinguished with difficulty in the laboratory. On one field a good crop of wheat was grown, followed by a good crop of clover and tame grasses. On the other field, the corresponding crops had been quite poor. The field yielding the good crops had been plowed somewhat deeper, and had previously received a moderate application of stable manure. Otherwise, so far as could be learned, the cultural history of the fields had been the same. For convenience, the sample from the first field will be designated "good," and from the other "poor."

Aqueous extracts from these soils were prepared, the same proportion of distilled water to soil being taken in each case, and the time of contact being the same. The solutions were freed from suspended matter by being passed through Pasteur-Chamberland bougies under pressure. Young wheat seedlings germinated at the same time, and selected carefully for uniformity of size and apparent vigor, were grown in these solutions for three days. At the expiration of this period the seedlings in the extract from the good soil were about five inches in height, and the roots were clear, clean and turgid. The plants in the poor extract were scarcely three inches in height, and the roots were assuming a slimy, unhealthy appearance and becoming flaccid at the tips. The plants were then all removed, the roots washed carefully in tap water; the plants which had been in the poor solution were placed in the good solution, and those which had been in the good solution were placed in the poor solution. At the end of four days further, the poor plants had surpassed in height the ones which had previously been in the good solution, and the roots had acquired the general characteristics of healthy plants. These which had been originally in the good solution and then transferred to the poor, had made little additional growth, and the roots had become somewhat flaccid.<sup>1</sup>

This experiment was repeated several times, not only with

<sup>1</sup> The success of this and of many of the following experiments was due in large measure to the skill and patience of Mr. James E. Breazeale.

the soils cited but with samples from adjacent good and poor spots in fields on several soil types from widely separated areas; for instance, Cecil clay from near Statesville, North Carolina; Sassafras loam from Maryland; Windsor sand from Delaware; and similar results were obtained. In other words, these water cultures produced plants which showed much the same differences, in kind and degree, as had been observed in the field. This was recognized as an important step forward, for it indicated that *whatever was making a difference in the crop-producing power of these soils in the field was transmitted to their aqueous extracts*, and methods for studying the chemical properties of solutions are far in advance of methods for studying mixtures of solids.

The soil extracts described above were subjected to a careful analysis for their mineral constituents. They were found to be practically identical in this respect. Further, the poor extract contained decidedly more nitrates than the good—from three to four times as much. It follows, therefore, that the difference in the soils which produced a good and a poor crop respectively, was not due to a difference in mineral plant nutrients, or other mineral differences probably, nor to their respective content of nitrates. Consequently, the poor solution was such, not because of the lack of anything, but because of the presence of something inimical or “toxic” to plant growth; and further, this something must be an organic substance or substances more or less soluble in water. This conclusion was confirmed in the following way.

Samples of the poor solution from the soil obtained near Statesville, N. C., were diluted twice, five times, and ten times, and wheat seedlings were grown in these solutions, using a sample of the good solution as a check. It was found after several days growth that the plants in the solution diluted tenfold were about as good, or perhaps slightly better, than those grown in the check solution. In every case diluting the poor solution had improved it for plant growth, and the higher the dilution the greater the improvement, in spite of the consequent dilution of the mineral plant nutrients. The only explanation of these

results which has yet suggested itself is that the toxic organic substances present were less effective on dilution until the concentration reached a point where they actually became stimulative, as is common with toxins of every character.

Another set of experiments confirmed the conclusion that the poor solution contained some organic substance inhibitory to plant growth. A number of water cultures was prepared from the aqueous extract of the poor soil, and lime in various forms was added to the cultures. To two of the cultures lime carbonate and lime sulphate respectively were added in excess, so that there was in each case a powdered solid at the bottom of the containing vessel. At the end of two days the wheat seedlings which were growing in the vessels containing the powdered solids had decidedly outstripped those growing in all the others, the tops having the appearance of unusually good and healthy plants. The roots were of a very remarkable character, being exceptionally long, very turgid, clear, clean and translucent.

At once, new experiments were carried out in which there were added to the poor solution, precipitated ferric hydroxide freed from all adhering salts, precipitated alumina, shredded filter-paper, absorbent cotton, or carbon black. In every case the same result was obtained as before, a much improved growth of top and a vastly better root development. Since, by no possibility could these various added substances have increased the concentration with respect to mineral nutrients, another explanation must be sought. Aside from their insolubility, the one property common to these various substances was the large amount of surface they brought into contact with the solution. The one obvious explanation of their effects on the growth of the wheat seedlings, therefore, is that they withdrew or absorbed from the solution some substance or substances deleterious to plant growth. As diluting with respect to mineral nutrients could not possibly be expected to improve the cultural value of the solution, the conclusion seems evident that the effect produced by these various absorbents was due to more or less complete removal from the solution of organic substances inhibitory

to plant growth. These experiments were then repeated in a modified form by shaking the poor solution with such absorbents as precipitated ferric oxide or carbon black and filtering before adding the seedling plants. The solutions thus prepared proved very satisfactory nutrient media, although the decided elongation of the roots, always observed when the absorbents were in contact with the solutions, was not so noticeable with these filtered solutions.

The experiments just described were repeated with extracts from a number of soils which were supporting or had recently supported poor crops. The accumulated mass of evidence admits of no doubt that in many cases the apparent lack of fertility of a soil is due to the presence of some organic substance or substances soluble in soil water. This point established, there was studied the effect of fertilizers when added to aqueous extracts from poor soils.

A large amount of experimenting has been done on this subject. It has been found that the common commercial fertilizers, as well as many other substances, when added to the soil extract containing growing plants, sometimes improve the plants, sometimes the contrary. But, in general, those particular substances which improve any given soil for a crop also improve the aqueous extract of the soil for the growth of the same crop plant; *i. e.*, should a soil be known to respond well to the application of superphosphates when planted to wheat, then the probability is great that the aqueous extract of the soil will be improved as a culture medium for the wheat plant by addition of calcium phosphate. Particularly important in this connection are certain experiments with organic fertilizers.

A soil which had been found to be quite unproductive with regard to wheat and ordinary tame grasses yielded, however, a much better growth of plants if pyrogallol or better pyrogallol and lime were added to the soil some days before planting. An aqueous extract of this soil tested with young wheat seedlings produced but a poor growth, as did the soil itself. But with the addition of pyrogallol or pyrogallol and lime to the soil ex-

tract, and especially if the extract so treated were allowed to stand for a few days with free access of air, there was obtained a culture medium which yielded remarkably good results with wheat seedlings. Not only was there an excellent and increased development of tops, but the roots of the seedlings grown in the solution treated with pyrogallop were unusually long, turgid, clear and translucent. Here, then, there was obtained an increased amount and improved character of growth by the addition of a substance which contained only carbon, hydrogen and oxygen, and no recognized plant food. Other organic substances, such for instance as tannin, gave similar results.

With the recognition that the presence of organic dissolved substances in the nutrient medium produced effects on a growing plant of as great or even greater magnitude than those produced by inorganic dissolved substances, there was carried out a number of experiments to test more specifically such substances as might reasonably be expected to be present naturally in soils. The results thus obtained suggested experiments with other related substances. The first substance to suggest itself is stable manure. Taking it all in all, this substance is probably the most efficient as well as the most generally used soil amendment in the experience of mankind. The good effects produced by this substance have in the past been generally considered as due to the readily "available" potash, phosphoric acid and nitrogen it contains, but thoughtful experimenters and agriculturists have long doubted that this explanation is sufficient, since, after all, the mineral constituents of stable manure are usually small in amount, and out of all proportion to the effects resulting from its use. That some of the results are due to an improvement in the physical condition of the soil when manure is used has quite rightly been generally assumed; but to its content of nitrogenous components its value has in the main been ascribed.

A well-fermented aqueous extract of stable manure was prepared, and filtered free of suspended solids. Four equal volumes of this solution were taken. Three of these portions were evaporated to dryness in platinum dishes, and the residues

incinerated. To the dishes containing the ash were added respectively nitric acid, sulphuric acid, and hydrochloric acid in slight excess, and the dishes again brought to dryness. Water cultures for wheat seedlings were then prepared.<sup>1</sup> Into one was introduced the given volume of manure extract; into another the ash from an equal volume of the extract which had subsequently been treated with nitric acid; and cultures with the ash which had been treated respectively with sulphuric and hydrochloric acid were similarly prepared. After ten days growth, the plants from the several cultures were compared. The plants from the cultures which contained the sulphates and the chlorides were not materially different from the plants grown in the check culture. The plants from the nitrate culture had larger shoots, but shorter roots than the check plants. But the plants grown in the culture to which the manure extract had been added directly had by far larger and better shoots and the roots were incomparably superior to those grown in any other culture, being larger, thicker, better branched, clear, bright and translucent, and very turgid, very like the roots obtained in cultures to which carbon black or precipitated ferric oxide had been added.

The results of this experiment, which has been repeated a number of times, using manure extracts of various origins, leave no doubt that it is the organic components of the manure which produce the characteristic effects, for the ash culture contained all and even more of the mineral constituents "available" in the original extract, and the nitrate culture excluded any explanation based on the nitrogenous content of the manure. This conclusion was supported by the results of another experiment.

To a manure extract was added alcohol, which precipitated most of the organic dissolved substances but very little of the inorganic ones. The precipitated organic matter was filtered off, dried carefully in a water oven to eliminate the alcohol, and then taken up in sufficient water to equal the original volume of manure extract. The filtrate containing the major part of the

<sup>1</sup> Further studies on the properties of unproductive soils, B. E. Livingston *et al.*, Bull. 36, 1907, and 48, 1908, Bureau of Soils, U. S. Dept. Agriculture.

salts was boiled vigorously to eliminate the alcohol and water was then added to restore the original concentration. A third solution was prepared by bringing together the organic and inorganic substances which had previously been separated as above described. The three solutions were used as water cultures for wheat seedlings, a solution of the original manure extract being taken for a check culture. The original manure extract and the reconstructed manure extract gave plants of about equal development. The culture containing the organic dissolved substances only, gave plants of nearly, but not quite, equal development to those grown in the check culture. But the plants grown in the solution containing the dissolved minerals only, while fine plants and making what would ordinarily be considered a good development, were decidedly smaller as regards their aerial parts, and the roots were in no wise comparable to the roots of the plants grown in the cultures containing the dissolved organic substances.

This last experiment has been repeated, with dissolved substances prepared from another manure extract, but in this case the organic and inorganic substances were separated by dialysis. This suggested yet another experiment, in which it was sought to hasten the process of dialysis, by introducing electrodes into the manure extract, each electrode being surrounded by some porous membrane, either of parchment paper, or unglazed porcelain. Not only were the mineral constituents of the manure extract readily separated in this way, passing into the electrode chambers, as did also to some slight extent organic compounds, but also about the outer walls of the electrode chambers there was marked segregation and deposition of organic materials. The organic substances deposited at the cathode were found to stimulate greatly the growth of wheat seedlings while those deposited at the anode were found to retard the growth of seedlings. It seems probable, therefore, that stable manure contains organic components which produce as great or greater effects upon growing plants as do the inorganic substances it contains: that on the whole these organic components induce

increased plant growth, but some of them, by themselves alone, would retard plant growth.

In a similar way green manures have been examined. If fresh clover, alfalfa, or cowpeas, be macerated and an aqueous extract thus prepared, it will in general be quite toxic to plants such as wheat; and if this extract be allowed to stand and ferment or sour the resulting solution will be totally unfit for the growth of seedling plants. But if the clover, alfalfa, or cow-pea vines be allowed to wilt thoroughly before being macerated and extracted, or if they be macerated and incorporated with soil and allowed to remain thus for ten days or a fortnight before being extracted; then, the resulting solution will be quite stimulating to such plants as wheat, corn or the grasses, when added either to water or soil cultures. It would seem, therefore, that the mineral constituents of the legumes commonly employed as green manures are less important than the organic, in affecting the growth of crops subsequently planted, and the inhibitory or toxic action of fresh green manure seems to be recognized in the common practice of waiting some days after turning under a green manure crop before seeding to a new crop.

The wilting of a green manure involves a darkening and some blackening of the mass, with apparently some absorption of oxygen. This fact has suggested a trial of other organic substances which show a decided ability to absorb oxygen. Among such substances, pyrogallol stands preëminent. It has been shown that when pyrogallol, or better pyrogallol and lime, is added to certain soils, naturally low in productive power, and allowed to stand for a few days, these soils are readily brought into good condition and support good crops of wheat, rye, or grasses. Pyrogallol in water cultures is rather toxic to wheat plants, even in quite dilute solutions. But if the aqueous solution of pyrogallol be allowed to stand exposed to the air, and better if the solution be made slightly alkaline as by the addition of lime, oxygen is absorbed, and a dark brown or blackened solution is soon formed, which is stimulating to wheat seedlings. Many experiments have indicated it to be a general rule that

soluble organic substances which are toxic to plant growth yield oxidation products which are harmless or positively beneficial.

The suggestion has been made that the well-known infertility of subsoils, when freshly turned up, is caused by the presence of alkaloids of the purine or codeine type, due to the activities of anaerobic bacteria. Water cultures and pot cultures show that while these substances do have a marked effect on plant growth, it is, frequently, quite beneficial; strychnine for example, in certain concentrations, produces a very decided stimulation in the growth of wheat seedlings. It is clear that some other explanation will have to be sought for the lack of fertility of subsoils.

A number of the substances which may be expected for one reason or another to be present in soils, have been investigated as to their effect on plants. In this connection may be cited the work of Livingston<sup>1</sup> and of Dachnowski,<sup>2</sup> who have studied the effect on vegetation of the organic substances dissolved in bog waters. In the following table are given the results obtained by growing wheat seedlings in solutions containing some one of a number of substances which might be expected to occur in a soil or to be derivatives of such substances. It will be observed that in the case of these dissolved organic substances, as has been repeatedly established with the inorganic ones, in concentrations sufficiently dilute not to be toxic, they generally show the opposite effect and appear to be stimulating.

<sup>1</sup> Physiological Properties of Bog Water, by B. E. Livingston, Bot. gaz., **39**, 348-355, (1905).

<sup>2</sup> The toxic property of bog water and bog soil, by Alfred Dachnowski, Bot. gaz., **46**, 130-143, (1908).

TABLE I.—EFFECT OF VARIOUS ORGANIC COMPOUNDS UPON THE GROWTH OF WHEAT PLANTS, WITH  
ESPECIAL REFERENCE TO THEIR TOXIC PROPERTIES<sup>1</sup>

Compound	Duration of experiment	Lowest concentration causing death	Lowest concentration causing injury	Concentration causing greatest stimulation	Remarks
	days	p. p. m.	p. p. m.	p. p. m.	
a Aspartic acid..... HOOC-CH <sub>2</sub> -CH(NH <sub>2</sub> )COOH.....	10	500	100	....	Normal growth in concentration below 100 p. p. m. No injury below 1,000 p. p. m.
b Asparagine..... NH <sub>2</sub> -OC-CH <sub>2</sub> -CH(NH <sub>2</sub> ) <sub>2</sub> -COOH.....	9	....	....	....	Tops of all plants good. Roots slightly injured at higher concentrations Only roots were injured at 500 p. p. m. No injurious action
c Glycocol, CH <sub>2</sub> (NH <sub>2</sub> ) <sub>2</sub> COOH.....	9	....	....	....	
d Alanine, CH <sub>3</sub> CH(NH <sub>2</sub> ) <sub>2</sub> COOH .....	10	....	500	25	
e Leucine, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(NH <sub>2</sub> ) <sub>2</sub> COOH .....	9	....	....	....	
f Tyrosine, C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH(NH <sub>2</sub> ) <sub>2</sub> COOH .....	11	....	100	....	
g Choline, (CH <sub>3</sub> ) <sub>3</sub> N <sub>+</sub> CH <sub>2</sub> CH <sub>2</sub> OH COO <sup>-</sup> .....	10	....	500	1	Roots affected more than tops

<sup>1</sup>Certain organic constituents of soils in relation to soil fertility, by Oswald Schreiner and Howard S. Reed; assisted by J. J. Skinner, Bull. No. 47, Bureau of Soils, U. S. Dept. Agriculture, 1907.

## THE SOIL SOLUTION

TABLE I.—(Continued)

Compound	Duration of experiment	Lowest concentration causing death	Lowest concentration causing injury	Concentration causing greatest stimulation	Remarks
	days	p. p. m.	p. p. m.	p. p. m.	
<i>h</i> Neurine, $(\text{CH}_2)_3\text{N} \begin{cases} \text{CH} : \text{CH}_2 \\ \text{OH} \end{cases}$ .....	9	250	25	....	
Neurine (neutralized) .....	8	250	25	....	
<i>i</i> Betaine, $(\text{CH}_3)_3\text{N} \begin{cases} \text{CH}_2\text{CO} \\ \text{O} \end{cases}$ .....	9	....	....	....	No injury
<i>j</i> Alloxan, $\text{CO} \begin{cases} \text{NH.CO} \\ \text{CO} \end{cases}$ .....	10	1,000	100	....	
<i>k</i> Guanine, $\text{NH.C.NH.CO.C.NH} \begin{cases} \text{C} \\ \text{N} \end{cases} \text{CHI} \dots$	12	....	....	....	Insoluble above 40 p. m. No harmful effects
<i>l</i> Xanthine, $\text{CO.NH.CO.C.NH} \begin{cases} \text{C} \\ \text{N} \end{cases} \text{CHI} \dots$	10	....	....	....	No injurious action.
<i>m</i> Guanidine, $\text{HN} : \text{C} \begin{cases} \text{NH}_2 \\ \text{NH} \end{cases} \dots$	9	100	1	....	
<i>n</i> Skatol, $\text{C}_6\text{H}_5 \begin{cases} \text{C.CH}_3 \\ \text{NH} \end{cases} \text{CHI} \dots$	9	200	50	....	Roots injured more than tops

TABLE I.—(Continued)

Compound	Duration of experiment	Lowest concentration causing death	Lowest concentration causing injury	Concentration causing greatest stimulation	Remarks
	days	p. p. m.	p. p. m.	p. p. m.	
<i>o</i> Pyridine, $C_5H_5N$	9	....	50	....	In solutions of 50 p. p. m. and less the root growth was normal.
Picoline, $C_5H_4N.CH_3$	7	1,000	500	100	
Piperidine, $\begin{array}{c} H_2C \\   \\ H_2C \diagup CH_2 \\   \\ H_2C \diagdown CH_2 \end{array}$	7	250	25	....	
Piperidine (neutralized)	7	100	25	1	
Quinolin, $\begin{array}{c} N \\   \\ C \end{array}$	6	500	5	....	
<i>p</i> Ricin	10	....	40	....	Insoluble above 50 p. p. m.
<i>q</i> Mucin	10	....	100	....	Not tested in concentrations higher than 100 p. p. m.

TABLE I.—(Continued)

Compound	Duration of experiment	Lowest concentration causing death	Lowest concentration causing injury	Concentration causing greatest stimulation	Remarks
	days	p. p. m.	p. p. m.	p. p. m.	
r Pyrocatechin, $C_6H_4(OH)_2$ (1,2) . . . . .	12	500	25	1	
s Arbutin, $C_{12}H_{16}O_7$ . . . . .	12	500	25	1	
t Phloroglucin, $C_6H_3(OH)_3$ (1,3,5) . . . . .	13	500	25	1	
u Vanillin, $C_6H_3\begin{cases} \diagdown \\ \diagup \end{cases} O.CH_3$ . . . . .	9	500	1	...	
Vanillic acid, $C_6H_3\begin{cases} \diagdown \\ \diagup \end{cases} O.CH_3$ . . . . .	7	100	25	5	
v Quinic acid, $C_6H_7(OH)_4COOH$ . . . . .	10	500	100	...	
w Quinone, $C_6H_4\begin{cases} \diagdown \\ \diagup \end{cases} O$ . . . . .	9	100	1	...	
x Cinnamic acid, $C_6H_5CH:CH.COOH$ . . . . .	8	100	25	...	
Sodium cinnamate . . . . .	12	...	100	...	
y Cumarin, $C_6H_4\begin{cases} \diagdown \\ \diagup \end{cases} O$ . . . . .	8	100	1	...	

Roots were stimulated in lower concentrations

TABLE I.—(Continued)

Compound	Duration of experiment days	Lowest concentration causing death p. p. m.	Lowest concentration causing injury p. p. m.	Concentration causing greatest stimulation p. p. m.	Remarks
<i>z</i> Daphnetin, $C_6H_{12}\begin{array}{c} \text{CH} : \text{CH}_2 \\ \diagdown \\ \text{O} \end{array} / \begin{array}{c} \text{O} \\ \diagup \\ (\text{OH})_2 \end{array} \dots\dots\dots\dots\dots\dots\dots$	12	....	50	....	Insoluble above 50 p. p. m. Roots somewhat injured
<i>aa</i> Esculin, $C_{15}H_{20}O_9$ ..... <i>bb</i> Piperonal (heliotropine) ..... $\begin{array}{c} C_6H_3-O \\ \diagup \\ \diagdown \\ O \end{array} \begin{array}{c} CH_2 \\ \diagup \\ \diagdown \\ O \end{array} \dots\dots\dots\dots\dots\dots\dots$	13	500	1	....	
<i>cc</i> Borneol, $C_{10}H_{18}(\text{OH})$ ..... <i>dd</i> Camphor, $C_{10}H_{16}O$ ..... <i>ee</i> Turpentine, $C_{10}H_{16}$ ..... $\begin{array}{c} C_6H_3-O \\ \diagup \\ \diagdown \\ O \end{array} \begin{array}{c} CH_2 \\ \diagup \\ \diagdown \\ O \end{array} \dots\dots\dots\dots\dots\dots\dots$	7	100	1	....	
	10	100	1	....	
	8	300	5	....	
	8	500	10	....	

- a. Aspartic acid has been found in young sugar-cane and in seedlings of the bean and pumpkin.
- b. Asparagine was first found in asparagus; but has since been shown to be relatively abundant in many species.
- c. Glycocol is one of the simpler and more common degradation products of proteins.
- d. Alanine is a common degradation product of proteins and is related chemically to phenylalanine, and to tyrosine, which has been found in many plants.
- e. Leucine, an amino-acid of a paraffine series and a decomposition product of proteids, has been found in certain mushrooms, vetches, lupine, gourds, potatoes, corn, etc.
- f. Tyrosine is an important decomposition product of proteids, is widely distributed and found in many plants and fungi.
- g. Choline is a derivative of certain lecithins and is found in many seeds and growing plants.
- h. Neurine is a substance closely related to choline, and probably formed from it.
- i. Betaine is closely related to both choline and neurine, and is found in many seeds and plants.
- j. Alloxan is closely related chemically to convicine, which latter is found in beets and certain beans.
- k. Guanine is a widely distributed nitrogenous body, and has been found in the seeds of vetch, alfalfa, clover, gourds, barley, sugar-beets and sugar-cane.
- l. Xanthine, a substance closely related to guanine, has been found in a number of plants.
- m. Guanidine, a substance chemically related to guanine, has been found in a number of plants of different species.
- n. Skatol is a derivative of proteids and is a common product of the activities of some varieties of bacteria.
- o. Pyridine has been shown to exist in soils, as such probably, by Shorey, who obtained it from certain soils in Hawaii.
- p. Ricin is found in the castor-oil plant.
- q. Mucin has been found in yams.
- r. Pyrocatechin has been found in the bark of various trees, the berries of the Virginia creeper, the sap of sugar beets and in several varieties of willows.
- s. Arbutin has been found in many plants, especially in some of the grasses.
- t. Phloroglucin is easily derived from a number of plant constituents.
- u. Vanillin forms readily from a glucoside, which is very widely distributed in many plants, and by some authorities is supposed to be a product of the decomposition of wood tissues.

v. Quinic acid, which is found with quinine in the cinchona bark, also occurs in beet leaves, certain bays, cranberry leaves, and occasionally in other plants.

w. Quinone has been shown to result from the action of a certain fungus, *Streptothrix chromogena*, common in soils.

x. Cinnamic acid is found in certain barks, and forms esters which have been found in the leaves of various plants.

y. Cumarin has been found in a large number of plants, including the grasses, beets, sweet clover, etc.

z. Daphnetin occurs in some species of *Daphne* and is closely related to cumarin.

aa. Esculetin, as well as the corresponding esculigin, has been found occasionally in a number of plants.

bb. Heliotropine, or piperonal, has the odor of heliotrope and is found in flowers.

cc. Borneol occurs in needles of different varieties of pine, fir, spruce and hemlock, golden rod and thyme.

dd. Camphor is closely related chemically to borneol and is secreted by a number of plants; it is found in the wood of *Cinnamomum*, cinnamon root, in the leaves of sassafras, spikenard, rosemary, rosewood, etc.

ee. Turpentine is a constituent of many plants and coniferous trees.

Finally, a number of organic substances has been isolated from soils. Their composition, and in several cases their constitutions have been determined. The effects of these on plants, when they are present in the cultural media have been studied. Thus, Shorey<sup>1</sup> was able to isolate picoline carboxylic acid ( $C_5H_7NO_2$ ) from certain soils in Hawaii, and this same substance has since been found in several soils of the United States. In aqueous solutions it is quite toxic to wheat seedlings. Since then a number of other definite organic compounds have been isolated from soils belonging to at least eight different classes of organic substances, including:<sup>2</sup>

Hentriacontane,  $C_{31}H_{60}$ .

Monohydroxystearic acid,  $CH_3(CH_2)_6CHOH(CH_2)_5COOH$ .

Dihydroxystearic acid,  $CH_3(CH_2)_7CHOHCHOH(CH_2)_7COOH$ .

<sup>1</sup> Organic nitrogen in Hawaiian soils, by E. C. Shorey, report of Hawaii Experiment Station, 1909, 37-50.

<sup>2</sup> Chemical Nature of Soil Organic Matter, by Oswald Schreiner and Edmund C. Shorey, Bull. 74, Bureau of Soils, U. S. Department of Agriculture, 1910.

- Agroceric acid,  $C_{21}H_{42}O_3$ .  
Paraffinic acid,  $C_{24}H_{48}O_2$ .  
Lignoceric acid,  $C_{24}H_{48}O_2$ .  
Phytosterol,  $C_{26}H_{44}O.H_2O$ .  
Pentosan,  $C_5H_8O_4$ .  
Agrosterol,  $C_{26}H_{44}O.H_2O$ .  
Picoline carboxylic acid,  $C_7H_7O_2N$ .  
Histidine,  $C_6H_9O_2N_3$ .  
Arginine,  $C_6H_{14}O_2N_4$ .  
Cytosine,  $C_4H_5ON_3.H_2O$ .  
Xanthine,  $C_5H_4O_2N_4$ .  
Hypoxanthine,  $C_5H_4ON_4$ .  
Glycerides, resin acids, etc.

Some of these, picoline carboxylic acid, dihydroxystearic acid and the pentosan just cited, are toxic to growing plants; others are not. The origin and mode of production of these substances in the soil is, generally speaking, uncertain and obscure, and is yet one of the important fundamental problems confronting the soil chemist.

It is important to note that the organic substances thus far isolated from soils are of widely varying types, and with very different chemical characteristics. As pointed out above, almost any type of organic substance is likely to be found in soils, and the effects of any of them on growing plants can hardly be predicted from *a priori* considerations.

It has been found that as a general rule the continued growth of one crop in any soil results in a low crop production. Pot cultures have given even more pronounced results in the same direction. The explanation long accepted is that the soil has, as a result of continued cropping, become deficient in some one or more of the "available" mineral nutrients. Pot experiments, where the garnered crop was returned to the soil and still a diminished yield was obtained, throw doubt on this explanation. Still further doubt results from water-cultures which, by growing a crop in them, become "poor" for subsequent crops, al-

though there is maintained in them an ample supply of mineral plant nutrients, and they are easily renovated by good absorbers. These facts find a more satisfactory explanation as being due to the production in the nutrient medium of deleterious organic substances originating in the growing plant itself. This idea seems to have been advanced first by De Candolle, in 1832,<sup>1</sup> to account for the beneficial results obtained by employing a rotation of crops. It appears to have been held by Liebig at one time, although he subsequently abandoned it in favor of the view that the benefits of a crop rotation are due to the several crops requiring different proportions of mineral nutrients, and that the disturbance of the balance in the soil produced by one crop is not unfavorable to the growth of some other crop. Although lacking direct experimental confirmation, this latter view of Liebig's has long prevailed among agricultural investigators, partly by reason of his authority, partly by reason of the dominance of the plant-food theory of fertilizers, and partly by reason of the fact that the ideas of De Candolle as originally advanced included certain errors soon detected. The trend of recent investigations has been distinctly in favor of a modified form of the view of De Candolle. It has been recognized that other factors enter into crop rotations, such as the elimination of associated weeds, various kinds of animal, insect and plant parasites, preparation of the soil by a deep-rooted crop for a shallow-rooted following crop, etc. It has come to be recognized that there are natural associations of plants, and natural rotations of vegetation certainly determined by other than plant-food factors. Thus, in the eastern United States, wheat is followed by ragweed naturally, while across the fence cocklebur and wild sunflower come in after the corn, the difference in vegetation being as sharply marked after the removal of the crops as when they still occupied the land. Analyses of the ragweed, for instance, although it is a shallower rooted crop than wheat, show that it takes from the soil as much of the

<sup>1</sup> See in this connection, Further studies on the properties of unproductive soils, by B. E. Livingston, Bull. No. 36, Bureau of soils, Dept. of Agric., 1907, p. 7-9.

mineral nutrients as does the preceding<sup>1</sup> wheat crop. The investigation of Lawes and Gilbert<sup>2</sup> on fairy rings showed that the continual widening of the rings can not be satisfactorily explained by the comparison of the mineral constituents in the soil within and without the rings. Work at Woburn<sup>3</sup> on the effect of grass on apple trees finds no other plausible explanation than that the growing grass produces in the soil organic substances detrimental to young apple trees. A number of similar cases have been recorded.

<sup>1</sup> Mr. J. G. Smith has made a comparison between the potash and phosphoric acid content of the wheat and following crop of ragweed grown on a farm in Fairfax Co., Va. His unpublished results, with some others found in the literature, are given in the following table:

Material	Potash $K_2O$ per cent.	Phosphoric acid, $P_2O_5$ per cent.	Analyst
Wheat .....	0.76	0.52	Smith
Young ragweed .....	1.78	0.73	Smith
Ragweed in seed .....	1.28	0.35	Smith
Ragweed in seed and accompanying plants .....	1.18	0.39	Smith
Winter wheat in flower....	1.796	0.51	Wolff's tables in Johnson's "How Crops Grow," p. 376.
Ragweed .....	1.79	0.41	DeRoode, in Bull. 19, W. Va. Agr. Exp. Sta., 1891
Ragweed .....	1.809	0.54	Burney, 2d. Ann. rept. S. C. Stat., 1889, p. 146

On the whole, ragweed seems to require and take from the soil about as much mineral matter as does wheat. It is stated by some of the dairy farmers near Washington, who cut the mixture of ragweed, other weeds and grass following wheat, for a hay crop, that the weight of the ragweed crop is generally heavier than that of the wheat crop. Therefore the ragweed actually removes more mineral matter from the field than does the wheat. These facts lend no support to the popular notion that wheat "exhausts" the soil of its "available" mineral plant nutrients. For analyses of a number of common American weeds, see Analyses of the ashes of certain weeds, by Francis P. Dunnington: Am. Chem. Jour., 2, 24-27, (1880).

<sup>2</sup> Note on the occurrence of "fairy rings," by J. H. Gilbert: Jour. Linn. Soc., 15, 17-24, (1875).

<sup>3</sup> Second, third and fifth reports of the Woburn Experimental Fruit Farm, 1900, 1903, 1905.

Finally, although less work has been done in this direction with higher plants than with other organisms, it is now recognized as a general law of all living organisms that they function less readily as the products of their activities accumulate.<sup>1</sup> These products may, however, be inimical, neutral or even stimulating to other organisms.

This problem has been investigated critically by direct ex-

<sup>1</sup> It may not be amiss to point out here that this general law holds for all dynamic phenomena. In chemistry, for instance, the general law is well recognized that the rate of reaction diminishes with increase in the active mass of the reaction products. It can be shown that the principle applies to plant growth. Young plants will withdraw potassium more rapidly than chlorine from solutions of potassium chloride; that is, the solution soon contains free hydrochloric acid. Conversely the plants cause a solution of sodium nitrate to become alkaline. Therefore, if the above principle holds, then the initial addition of small amounts of hydrochloric acid to a solution of potassium chloride should slow up the absorption of potassium by seedling wheat plants, or the addition of sodium hydroxide the absorption of nitrogen from a solution of sodium nitrate. Mr. J. J. Skinner has tested this idea with the following results, growing carefully selected wheat seedlings, for 3 days in solutions of pure potassium chloride, solutions of potassium chloride containing initially enough excess of hydrochloric acid to be of an N/5,000 concentration with respect to the acid, solutions of sodium nitrate, and solutions of sodium nitrate containing initially an excess of sodium hydroxide.

Solutions of KCl containing 80 p. p. m. K<sub>2</sub>O.

- 1 K<sub>2</sub>O absorbed 40.0 p. p. m.
- 2 K<sub>2</sub>O absorbed 40.0 p. p. m.
- 3 K<sub>2</sub>O absorbed 36.3 p. p. m.

Solutions of KCl (80 p. p. m. K<sub>2</sub>O) and HCl (N/5,000).

- 4 K<sub>2</sub>O absorbed 26.7 p. p. m.
- 5 K<sub>2</sub>O absorbed 29.5 p. p. m.
- 6 K<sub>2</sub>O absorbed 26.7 p. p. m.

Solutions of NaNO<sub>3</sub> containing 80 p. p. m. NH<sub>3</sub>.

- 7 NH<sub>3</sub> absorbed 30.2 p. p. m.
- 8 NH<sub>3</sub> absorbed 30.2 p. p. m.
- 9 NH<sub>3</sub> absorbed 32.5 p. p. m.

Solutions of NaNO<sub>3</sub> (80 p. p. m. NH<sub>3</sub>) and NaOH (N/5,000).

- 10 NH<sub>3</sub> absorbed 27.8 p. p. m.
- 11 NH<sub>3</sub> absorbed 34.3 p. p. m.
- 12 NH<sub>3</sub> absorbed 27.8 p. p. m.

perimentation, growing wheat, and other seedlings in water and agar cultures.<sup>1</sup> It has been shown that wheat renders the culture media unsuitable for subsequent wheat crops, though it can be reclaimed or renovated by treatment with such absorbents as carbon black, or by other methods.<sup>2</sup> Wheat did about as well when grown in a medium which had previously supported a growth of cowpeas as when planted in a fresh medium; poorer results were obtained after oats; no crop produced such poor results in the succeeding wheat crop as did wheat itself.

It is yet a matter of dispute as to whether the substances thus added to nutrient media are truly excretory products of the plant, sloughed off or otherwise eliminated from the surface of the roots, or further elaborated by bacterial or other agencies before becoming effective. These are important problems for the plant physiologist and the soil chemist alike. It is beyond dispute, however, by reason of a large and increasing weight of evidence, much of it direct experiment, that, as a result of the growing of plants, soils and the soil water do contain organic substances; harmful to the plant or organism eliminating them; harmful, innocuous, or even stimulating to other plants or organisms.

For the elimination from the soil of toxic or inhibitory organic substances, whether excreted by roots or otherwise produced, several methods are more or less effective. When, as is sometimes the case, the substance is volatile, it may be removed by heating, distilling with steam, or passing a current of air through the soil or cultural medium. These methods, while effective in the laboratory and possibly applicable to greenhouse conditions, are naturally inapplicable to field conditions. In this last case the obvious procedure is to increase as much as possible the absorptive powers of the soil; to secure the best possible drainage; and with these, the best possible aeration of the soil.

<sup>1</sup> Some factors in soil fertility, by Oswald Schreiner and Howard S. Reed, Bull. No. 40, Bureau of Soils, U. S. Dept. Agriculture, 1907.

<sup>2</sup> Soil fatigue caused by organic compounds, by Oswald Schreiner and M. X. Sullivan: Jour. Biol. Chem., 6, 39-50, (1909).

It has been found that, in general, a cultural medium which has been rendered unfit for the continued growth of a crop, is readily renovated by treatment with oxidizing agents, and is sometimes rendered even better than ever by such treatment, which would suggest that the oxidation products from plant effluvia may be even beneficial to the plant. To this end the growing plant seems itself to be an active agent, apparently attempting automatically to protect itself against the products of its own activities. It has been pointed out by Molisch<sup>1</sup> that root secretions have an oxidizing power, apparently of an enzymatic character. Some doubt of the validity of Molisch's work has been raised by Czapek, Pfeffer, and others; nevertheless it is now accepted that while intercellular autoxidation or reduction processes may take place in living roots, the higher plants, such as our common crop plants, also show a more or less well-developed extracellular oxidizing power in the neighborhood of the root tips and root hairs.<sup>2</sup> That this oxidizing power displayed by growing roots is enzymatic is indicated by the fact that artificial culture media frequently display it also after plants have been grown in them for a short while.<sup>3</sup>

It has been shown that the oxidizing action of growing roots is generally promoted by having the cultural medium slightly

<sup>1</sup> Über Wurzelausscheidungen und deren Einwirkung auf organische Substanzen, von Hans Molisch. Sitzungsber. Akad. Wiss. Wien, Math. nat. Kl., **96**, 84-109 (1888).

<sup>2</sup> The rôle of oxidation in soil fertility, by Oswald Schreiner and Howard S. Reed: Bull. No. 56, Bureau of Soils, U. S. Dept. Agriculture, 1909.

<sup>3</sup> From considerations as yet highly speculative, a different type of oxidation by roots might be anticipated. It is recognized that in the absorption of mineral nutrients by plants a certain amount of selection enters. For example, a plant with its roots in a solution of potassium chloride, absorbs more potassium than chlorine, relatively, and free hydrochloric acid is left in the solution. Obviously in the absorption, work is done, and a possible explanation is that water is decomposed at the absorbing surface of the root, with the liberation of oxygen. Theoretically, it ought not to be difficult to investigate this by a study of the energy changes during absorption, but growing plants do not lend themselves readily to such experimentation.

alkaline or neutral rather than acid. It is also promoted by the addition of various mineral salts, notably by nitrates, phosphates, or lime salts. Potassium salts promote the oxidation but slightly, and in some experiments have even produced a slight decrease. The corresponding sodium and ammonium salts are more favorable than those of potassium.<sup>1</sup> It appears altogether probable, therefore, that the mineral salts in commercial fertilizers may have some importance in this connection.

Whatever may be the role of mineral fertilizers towards organic substances toxic to growing plants, it is certain that they have an importance and one that is probably specific, as indicated by some recent investigations.<sup>2</sup> Culture solutions containing the constituents potassium, nitric acid and phosphoric acid were prepared in such manner that they covered the range of all possible ratios of these constituents in intervals of ten per cent. in each. Into one set of these solutions was introduced dihydroxystearic acid, into another set cumarin, and into a third set, vanillin, and into a fourth set, quinone. The growth of wheat seedlings in these several sets showed indubitably that these several organic substances which are all deterrent to the growth of wheat, were modified in their influence by the presence of the mineral salts; but that nitrates were more efficient than the other minerals in the case of the solutions containing dihydroxystearic acid or vanillin; phosphates were most efficient in the case of the solutions containing cumarin, and potassium most efficient in solutions containing quinone. As the organic substances used in these experiments, either in themselves or as typifying classes of compounds, may be anticipated in soils under natural conditions, it is again apparent that mineral fertilizers have a function in addition to the traditional one of increasing the supply of mineral nutrients.

The fact that the oxidizing power of roots is more marked when grown in aqueous extracts of soils in good tilth than in extracts made from soils in poor tilth, shows that cultural meth-

<sup>1</sup> Action of fertilizing salts on plant enzymes, by M. X. Sullivan, Jour. biol. chem., 6, (1909), proceed. XLIV.

<sup>2</sup> Private communication by Dr. Oswald Schreiner and Mr. J. J. Skinner.

ods are no less important in field practice than are fertilizers in promoting this important activity of plants. There is little reason to doubt that oxidizing agencies other than plant roots (bacterial for instance) are more or less active in every arable soil, and numerous investigations, among which Russell's researches<sup>1</sup> are conspicuous, leave little doubt that oxidation processes are promoted by good tilth. It is apparent, therefore, that by the activities of the plant itself as well as other agencies, the general tendency in soils is the destruction of or rendering innocuous harmful plant effluvia or other organic substances, and to this end are effective each of the three methods of soil control generally practiced, namely, tillage, crop rotation and fertilizers.

Among the organic components of the soil none have greater importance and interest than those containing nitrogen or as they are frequently called the nitrogen carriers. Conspicuous among these are the nitrates. While it is now generally conceded that ammonia and other nitrogen compounds can be taken up by higher plants and elaborated by them under special conditions, it nevertheless remains true that plants draw their needed supplies of nitrogen from the soil solution, mainly in the form of nitrates. The problems presented by these nitrogen carriers are mainly bacterial<sup>2</sup> and physiological, but certain features are of direct importance to the soil chemist and to a study of the soil solution. It is now known generally that there are many kinds of nitrifying and denitrifying bacteria in soils, and that probably every arable soil contains several species, or varieties at least of both kinds. With good tilth and consequent aerobic conditions, nitrifying processes prevail, and with poor

<sup>1</sup> Oxidation in soils, and its connection with fertility, by Edward J. Russell; *Jour. Agric. Sci.*, **1**, 261-279, (1905); Pt. II. The influence of partial sterilization, by Francis V. Darbshire and Edward J. Russell, **2**, 305-326, (1907).

<sup>2</sup> The fixation of atmospheric nitrogen by bacteria, by J. G. Lipman, *Bull.* **81**, Bureau of Chemistry, U. S. Dept. of Agriculture, 1904, p. 146-160; A review of investigations in soil bacteriology, by Edward B. Voorhees and Jacob G. Lipman, *Bull.* **194**, Office of Experiment Stations, U. S. Dept. of Agriculture, 1907.

tilth or in subsoils, anaerobic conditions and denitrifying processes prevail. Warmth, moisture, the reaction of the soil, and perhaps other factors markedly affect the activity of the organisms of the soil solution. Another important factor is that the absorptive powers of the higher plants are markedly affected by sunlight, so that, especially on bright and clear days, there is generally a higher concentration of nitrates in the soil solution in the morning than in the evening. This fact would seem to affect seriously the value of some recent and extensive investigations where it has been sought to classify soils by their content of water-dissolved nitrates. Nitric acid is more readily leached from soils than are most other acid radicals. Consequently nitrates, like other organic components of the soil solution, and unlike inorganic components, tend to vary greatly in concentration.

## **Chapter XII.**

### **FERTILIZERS.**

It is generally recognized that the great practical problem confronting the soil chemist is the proper use of soil amendments or fertilizers. The farmers of the United States now spend annually for fertilizers upwards of \$100,000,000. It is estimated by various authorities that a large fraction, perhaps as much as three-fourths, of the material represented by this expenditure is misapplied for lack of intelligent direction. Yet all of this enormous mass of fertilizers can be used to advantage. Great as it is, it is relatively small beside the total which will, and must, be used in a not distant future, with the growth and development of intensive methods of cultivation consequent upon the rapid settling of the country, the practical disappearance of new lands and the increase in money value of the old lands. The commercial importance of the problem, therefore, makes it desirable that special emphasis should be given to fertilizers from the point of view developed in the preceding chapters. It should be recalled that the use of fertilizers constitutes one of the three great general methods of soil control, and further that while tillage methods, crop rotations, and fertilizer applications can be used to supplement one another, no one of these methods can be expected to take satisfactorily the place of another.

Crop production is dependent upon a large number of factors. Upon the rainfall, both as to the amount and distribution; upon the sunlight, as to amount and distribution; upon the chemical and physical properties of the soil; soil bacteria and other biological agents; enzymes in the soil; biological factors in the plant, and probably many other things. Opinions do and will continue to differ as to what these factors are, but at least every one agrees that they are many.

Attempting to formulate these factors develops fundamental difficulties, since it is not positively known how far the variables are dependent or independent, and we have no idea as to the nature of the function or functions. The weight of existing evi-

dence favors the view that all the factors are dependent variables, although numerous attempts have been made from time to time to show that some one factor, such as the rainfall for instance, or the mean annual temperature, or available plant-food, is *practically* an independent factor. Although it should be rather easy to determine experimentally the nature of the function, if any of these various factors were independent, this has never been done, and this fact is itself a strong argument that all the factors in crop production are dependent on one another.

When there is introduced into the equation a factor for any one of the methods of soil control, *i. e.*, tillage, crop rotation, or fertilizers, it becomes even more apparent that the function is determined by dependent variables, for the new factor always more or less affects several if not all of those already cited. For instance, fertilizers certainly affect the chemical properties of the soil, its physical properties, the soil bacteria, perhaps the plant-food supply, the oxidation of plant effluvia and other factors. It is obvious, therefore, that a satisfactory theory of fertilizer action can not be a simple one but must of necessity be complex; and the same statement is no less true as regards tillage and crop rotation.

The recognition of the fact that the action of fertilizers is a complex function depending upon many factors and groups of factors which vary among themselves and with each individual soil, carries with it the conviction that an exact or quantitative fertilizer practice, while theoretically possible, is probably unattainable since methods for the solution of such complex functions are generally wanting. It is not surprising, therefore, that the empirical experience of the past has failed to develop a quantitative practice. However disappointing this may seem at first sight, the prospect is not altogether hopeless, for this point of view indicates a systematic scheme for experimentally determining a qualitative, but nevertheless rational, fertilizer practice. The dominance of the plant-food theory of fertilizers in the past, shutting off, as it has, a rational attack of the problem, is causing the annual waste of millions of dollars in misapplied fertilizers, and it is of scarcely less economic than sci-

tific importance to investigate and extend our knowledge of the effect of soil amendments upon the many factors in crop production. With a knowledge of the effect of fertilizers upon the physical, chemical and biological factors in crop production, and of the nature of the interdependence of these factors, will come the ability to manage intelligently the individual field for the particular crop. This knowledge can only come by attacking the problem from the dynamic view-point, and so far as the soil factors are concerned, they can apparently be studied best as they affect the properties of the soil solution.

While it seems certain that some fertilizer effects are directly upon the soil and secondarily upon the plants, it cannot be doubted that in others, the phenomena are more directly concerned with the absorption by and the metabolism within the plant and until these plant processes are better understood, nothing approaching a satisfactory practice can be anticipated. Why and how plants exercise the selective powers they appear to possess are fundamental questions yet to be answered. The important effects sometimes produced by adding to the nutrient medium such substances as manganese salts which are not necessary to the growth of the plant, can no more be neglected than the study of the phosphorus needs. The presence in the soil universally of substances other than the recognized mineral nutrients,<sup>1</sup> may very well have a significance for plant production hitherto unsuspected, for the fact that an organism can continue to function in the absence of a substance is no argument, much less proof, that it would not function better with that substance present. Recent investigations, showing that animal organisms are sometimes more resistant to certain toxins and diseases under starvation conditions or when ingesting substances unnecessary to normal development, suggest the possibility at least of similar phenomena with plants. It is at any rate clear that the practical problem of the best production of plants from soils is not merely one of providing a relatively large supply of potassium, phosphorus and nitrogen.

<sup>1</sup> See, for instance, Barium in soils, by G. H. Faileyer, Bull. No. 71, Bureau of Soils, U. S. Dept. of Agriculture, 1910.

In this connection it is well to consider what constitutes a commercial fertilizer. It must be a substance the addition of which either directly or indirectly affects the properties of the soil or the growing plant; it must be obtainable in large quantities and from a source or sources of supply not readily exhausted; and it must be cheap. Of the many substances filling the first condition, all those which fulfill also the other conditions are used as fertilizers, with the exception of common salt and human excrement. In spite of the fact that it does not contain a conventional plant-food, sodium chlorid appears to produce results quite similar to those produced by the usual fertilizer salts. Its use has been followed generally by an increased yield of crop, but occasionally by a decreased one, and it appears not improbable that further investigation would show sodium chloride to have a considerable value as a fertilizer. Human excrement or night soil, and the sewage and garbage refuse of our large cities are not commercial fertilizers, although having undoubtedly a high agricultural value. Objection has been urged to them that they are "filthy" and liable to contain dangerous pathogenic organisms. Both objections could be met. It seems a more rational explanation that the agricultural methods of this country have not yet become sufficiently intensive to necessitate the conservation of such materials or to justify their commercial exploitation.

New products will come into use from time to time, as in the case of calcium cyanamid and basic calcium nitrate. But it is worthy of note that these substances have become available not so much because of their agricultural value, but incidentally to the efforts of inventors and manufacturers to produce cheap nitric acid for the preparation of high explosives.<sup>1</sup> There "seems

<sup>1</sup> In this connection it may be of interest to call attention to the fact that the Twelfth Census shows less than a fifth of the sodium nitrate brought into the United States goes into the fertilizer trade. Moreover, the production of ammonium salts by the extensive coke and gas plants of the country has been practically *nil* not because of any inherent difficulties in making them or because the cost of production has been high, but because the market demands in this country have been too small.

no reason to doubt that an ample supply of desirable substances will always be available for fertilizer purposes. The immediate practical problem for the future is not the seeking of new fertilizers but the rational use of those at hand.

## Chapter XIII.

### ALKALI.

In the preceding chapters there have been considered the phenomena which obtain under humid conditions. Under exceptional conditions of prolonged drought there occurs an accumulation of soluble mineral substances at or near the surface of the soil. This phenomenon is pronounced in arid and semi-arid regions,<sup>1</sup> and the accumulations of soluble salts occurring in such regions is known in the United States as "alkali," in India as "reh," in Africa as "brak," and in other countries by various local designations. The study of the extreme conditions producing alkali has added materially to the present knowledge of the processes taking place in soil of humid areas. Moreover, alkali-infested areas are themselves becoming of so much importance with the growing needs for further new lands, that it seems wise to give here an outline of the chemical principles involved in their soil solutions.<sup>2</sup>

Alkali is sometimes a single salt, but usually a mixture of some two or more of the chlorides, sulphates, carbonates, bicarbonates, and occasionally the nitrates, phosphates and borates, of sodium, magnesium, potassium, and calcium, and occasionally strontium and lithium. In the United States, when the carbonate of sodium is present to an appreciable extent, the salt mixture is known as *black alkali*, in contradistinction to *white alkali*, which latter does not contain sodium carbonate.<sup>3</sup> Generally, but not

<sup>1</sup> Occasional occurrence of alkali in humid regions, by Frank K. Cameron, Bull. No. 17, Bureau of Soils, U. S. Dept. Agriculture, 1901, p. 36-38. This phenomenon should not be confused with the surface deposition of various kinds of saline material from springs, which is fairly common in both humid and arid regions, the world over.

<sup>2</sup> Alkali soils of the United States, by Clarence W. Dorsey, Bull. No. 35, Bureau of Soils, U. S. Dept. Agriculture, 1906.

<sup>3</sup> Black alkali is so called because the caustic solution containing sodium carbonate, in rising to the surface of the soil, dissolves and carries with it organic matter which is subsequently left on the surface in more or less blackish deposits, often ring-like in appearance. It is by no means uncommon, however, to find deposits of "black alkali" which are not black at all, and it is quite common to find "white alkali" so dark in color as to suggest the presence of sodium carbonate, although the latter be absent.

always, soils containing alkali also contain accumulations of the less soluble salts, calcium carbonate, or calcium sulphate, or a mixture of the two. These substances, sometimes cementing the less soluble mineral components of the soil, sometimes almost pure, are found in layers more or less continuous, and from a fraction of an inch to several feet in thickness, in a position approximately parallel to and at a moderate depth below the surface of the soil. In such cases these layers form a "hard-pan" and frequently the treatment of this type of hard-pan is the most difficult and vexing problem in the management of alkali-bearing soils.

The origin of alkali is often uncertain. In some cases the geological evidences in the area make it certain that the alkali came from the desiccation of former bodies of sea water which had become isolated from the ocean. In other cases the alkali appears to come from the desiccation of lakes which are the depositories of the drainage of a surrounding area, and which have no outlet to the sea. In still other cases it has been supposed that the alkali is derived from wind-borne sea-spray. Various explanations of a more or less special character with regard to particular localities or circumstances are to be found in the literature.<sup>1</sup>

The chemical principles involved in the desiccation of a body of sea water are now pretty well understood, owing mainly to the investigations of van't Hoff, Meyerhoffer, and their co-workers.<sup>2</sup> The salts in sea water and those constituting "white alkali" are mainly the chlorides and sulphates of sodium, potas-

<sup>1</sup> An interesting case is the Billings Area, Montana, where the alkali seems to be derived from the oxidation, solution and subsequent hydrolysis of the pyrites and marcasite of the neighboring Pierre shales. The sulphuric acid thus formed, leaching through shales and sandstones, takes up various bases and the predominating salts in the alkali of this area are the sulphates of sodium and magnesium.

<sup>2</sup> Zur Bildung der ozeanischen Salzablagerungen, von J. H. van't Hoff, Braunschweig, 1905-09. For a detailed discussion of these results with reference to alkali deposits see: Calcium sulphate in aqueous solutions, by Frank K. Cameron and James M. Bell, Bull. No. 33, Bureau of Soils, U. S. Dept. Agriculture, 1906.

sium and magnesium. Calcium is also present, appearing in deep deposits as anhydrite, and at the surface as gypsum.

From the results of this work it is possible to predict the order in which the different salts or minerals will separate from the evaporating solution. At ordinary temperature ( $25^{\circ}$  C) the first salt to be deposited from the dilute solution is *gypsum* ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) followed by *halite* or *sodium chloride* ( $\text{NaCl}$ ) in quantity. Sodium chloride continues to separate at all higher concentrations. Next will be deposited *kainite* ( $\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$ ). At the concentration then reached, the stable sulphate of calcium is *anhydrite* ( $\text{CaSO}_4$ ), which continues to separate from solution as desiccation proceeds. Consequently, if the gypsum previously deposited is yet in contact with the solution, it tends to be transformed to anhydrite and at all higher concentrations the deposition of anhydrite may be expected. As evaporation proceeds a point is reached where *kainite* and *kieserite* ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ) separate. Further evaporation brings a concentration at which *kieserite*, *carnallite* ( $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ ) are precipitated, and as the process proceeds, finally the point is reached where *kieserite*, *carnallite* and *bischofite* ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) all three separate with sodium chloride. The final products separating at a higher temperature,  $83^{\circ}$  C., are the same four solids, sodium chloride, kieserite, carnallite and bischofite.<sup>1</sup> The alternate layers of anhydrite and sodium chloride noticeable in some desiccated sea beds is probably the result of alterations in temperature, anhydrite being less soluble,

<sup>1</sup> It will be interesting to compare with the above the following brief description of the Stassfurt salt deposits, taken from Ries's Economic Geology of the United States, (1905), p. 127. "At the bottom is the main bed of rock salt which is broken up into layers 2-5 inches thick by layers of anhydrite. Above this come 200 feet of rock salt, with which are mixed layers of magnesium chloride and polyhalite. Resting on this is 180 feet of rock salt, with alternating layers of sulphates chiefly kieserite, the sulphate of magnesia. These layers are about 1 foot thick. Lastly, and uppermost, is a 135-foot bed consisting of a series of reddish layers of rock salts of magnesia and potassium, kainite . . . kieserite . . . carnallite . . . tachhydrite . . . as well as masses of snow-white boracite."

and sodium chloride somewhat more soluble in hot than in cold water. During warm weather there would be a greater tendency for anhydrite to separate and in colder weather for sodium chloride to be precipitated. Anhydrite at the surface would gradually absorb water vapor from the atmosphere and be transformed to gypsum.<sup>1</sup>

Besides the principal salts just described, there may separate at one concentration or another other various double salts including *langbeinite* ( $2\text{MgSO}_4\text{K}_2\text{SO}_4$ ), *polyhalite* ( $\text{K}_2\text{SO}_4\text{MgSO}_4\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ ), *glauberite* ( $\text{CaSO}_4\text{Na}_2\text{SO}_4\text{H}_2\text{O}$ ), *syngenite* ( $(\text{CaSO}_4\text{K}_2\text{SO}_4\text{H}_2\text{O})$ ), *potassium pentasulphate* ( $\text{K}_2\text{SO}_4\cdot 5\text{CaSO}_4\text{H}_2\text{O}$ ), *krugite* ( $4\text{CaSO}_4\text{K}_2\text{SO}_4\text{MgSO}_4\cdot 2\text{H}_2\text{O}$ ), and possibly others. These are all stable over very restricted ranges of concentration, however, and if formed, probably seldom persist, but pass over to more stable salts as the desiccation proceeds, and have little more than a passing theoretical interest.

The addition of carbonates to the system introduces some further modifications.<sup>2</sup> In this case lime carbonate is the first salt to be precipitated, followed probably by the same order of deposition as outlined above. As the mother liquor becomes more concentrated, it apparently loses its alkaline character, for the addition of an aleoholic solution of phenolphthalein does not produce the characteristic red color. That the solution does actually contain dissolved carbonates is shown by the appearance of the red color on diluting a portion of the mother liquor with distilled water. An interesting example in nature is furnished by the Great Salt Lake, Utah. A test of the water of this lake in 1899 gave no alkaline reaction with phenolphthalein.

<sup>1</sup> As examples, some of the gypsum deposits of Kansas may be cited, according to Haworth, Mineral resources of Kansas, 1897, p. 61, and the classical case at Bex, Switzerland, described by J. G. F. Charpentier, Über die Salz-Lagerstätte von Bex: Ann. Phys. Chim., 3, 75-80, (1825), and by G. Bischof, Elements of chemical and physical geology, London, 1854-58, Vol. 1, p. 350-1.

<sup>2</sup> The action of water and aqueous solutions upon soil carbonates, by Frank K. Cameron and James M. Bell, Bull. No. 49, Bureau of Soils, U. S. Dept. Agriculture, 1907.

but the reaction appeared promptly when distilled water was added, and further examination showed the water to contain about 0.012 per cent. sodium carbonate.<sup>1</sup> Slosson has reported similar cases in Wyoming.<sup>2</sup>

One "black alkali" system has been studied with some approach towards completeness.<sup>3</sup> In this case magnesium and potassium salts are not present, the system being composed of water, carbon dioxide, chlorides, sulphates, sodium and calcium salts, with the condition imposed, that the bases are present in amounts more than equivalent to the sulphuric and hydrochloric acids. On desiccation at 25° C calcium carbonate first appears followed by gypsum and then sodium sulphate decahydrate. Next appears a double salt ( $2\text{CaSO}_4 \cdot 3\text{Na}_2\text{SO}_4$ ) followed by anhydrous sodium sulphate, the Glauber's salt which formerly crystallized being no longer stable. Sodium chloride then precipitates and the concentration finally reaches a point where gypsum is no longer stable, and the final group of salts in contact with the evaporating solution under conditions of stable equilibrium consists of calcium carbonate, the double sulphate of soda and lime, anhydrous sodium sulphate and sodium chloride.

The desiccation of a lake which serves as the final repository of a regional drainage involves essentially the principles just discussed.<sup>4</sup> The constituents involved are the same. A serious

<sup>1</sup> Application of the theory of solutions to study of soils, by F. K. Cameron, Report No. 64, Field Operations of the Bureau of Soils, 1890, p. 149.

<sup>2</sup> Alkali lakes and deposits, by W. C. Knight and E. E. Slosson, Bull. No. 49, Wyoming Agr. Expt. Station, 1901, p. 108.

<sup>3</sup> The solubility of certain salts present in alkali soils, by Frank K. Cameron, J. M. Bell and W. O. Robinson, Jour. Phys. Chem., 11, 396-420, (1907).

<sup>4</sup> It has been suggested that the fact that shales or similar geological deposits are frequently to be found near alkali areas, indicates that the shales are the principal sources of the alkali. It is supposed that the constituents of the alkali salts were formed by the action of water on the shale minerals at or about the time the shales were deposited, and carried down with the latter. Subsequently the alkali has been leached out to appear at the surface of soils, generally at a lower level than are the shales.

problem involved in the consideration of this source of "alkali" is the high ratio of chlorine to the other constituents, in view of its very low ratio in the rocks from which it comes. The explanation undoubtedly involves the fact that the carbonates and sulphates are constantly being removed as calcium salts from a body of water which is more or less continuously receiving the drainage of any considerable watershed, and is at the same time subject to a relatively high rate of evaporation. The chlorine forming only very soluble salts under such conditions would be segregated and concentrated in the residual mother liquor. Most difficult is it to account for the relatively high ratio of sodium to potassium in alkali from such an origin. Some light is thrown on the subject by the progressive changes in concentration of a lake water which receives a regional drainage under arid conditions. To this end are given the following results of analyses of the waters of Utah Lake, made at different times<sup>1</sup> over an interval of twenty years, and showing that there is a segregation of chlorine and sodium taking place, although in this case the lake has an outlet in the Jordan River.

ANALYSES OF THE WATER OF UTAH LAKE. RESULTS IN PARTS  
PER MILLION

	Clarke 1883	Cameron 1899	Brown 1903	Seidell 1904 <sup>2</sup>	Brown 1904 <sup>3</sup>
Ca.....	55.8	67.6	80	67.7	67
Sr.....	—	—	—	1.7	—
Mg.....	18.6	13.8	92	73.5	86
Na.....	17.7	233.7	247	207.2	230
K.....	? ?	? ?	30	25.8	22
Li.....	—	—	—	0.7	—
SO <sub>4</sub> .....	130.6	236.7	365	332.9	378
Cl.....	12.4	316.5	336	288.5	337
HCO <sub>3</sub> .....	—	—	266	205.5	194
CO <sub>3</sub> .....	60.9	23.7	—	24.0	11
SiO <sub>2</sub> .....	10.0	—	—	22.6	28
Total .....	306.0	892.0	1416	1250.1	1353

<sup>1</sup> The water of Utah Lake, by F. K. Cameron: Jour. Am. Chem. Soc., 27, 113-116, (1905).

<sup>2</sup> Sample collected May 18. Lake unusually high.

<sup>3</sup> Sample collected Aug. 31. Lake still high for that season of the year.

The third general origin of alkali supposes that wind-borne sea-spray carries into the air salts which are left in very fine particles on the evaporation of the water, or are deposited on the ordinary atmospheric dust and carried over the land; and that this dust is precipitated here and there as may be determined by the various meteorological conditions which it encounters. All the land surface is supposed to be receiving more or less of it from time to time, but in arid regions the rainfall and drainage is not sufficient to return to the sea as much as is received therefrom.<sup>1</sup>

It is very probable that wind-borne salts from the sea are being carried over and to some extent being deposited on all the land surfaces of the earth. To what extent this process is taking place, and whether it is sufficient to account for the alkali of any particular region, available data fail to answer satisfactorily. Probably it is always associated with one of the origins of alkali already discussed and is in itself generally of secondary importance.

An argument frequently advanced against the validity of the hypothesis that wind-borne sea-spray is the origin of alkali is that the relative proportions of the several constituents in "alkali" are seldom if ever those obtaining in sea water. This argument does not take into consideration, however, that the several salts in the spray probably separate into crystals of widely different size and specific gravities, and there may well be taking place a selective or sorting action by the wind. More important, undoubtedly, is the selective action taking place in the soil itself; it can only be an accidental coincidence that the constituents of alkali in any particular occurrence should have the same quantitative relations as in the material from which it originated, no matter what may have been the nature of its origin.

In the field, alkali is found in a bewildering array of forms and types. Quite different combinations of constituents may be found in the same field within a few rods or even a few feet,

<sup>1</sup> For a recent interesting and valuable discussion of this subject with reference to a particular area, see: The origin of the salt deposits of Rajputana, by Sir Thomas H. Holland and W. A. K. Christie, Records of the Geological Survey of India, 38, 154-186, (1909).

and each case appears to have a distinct origin, to be in fact a law unto itself. Each alkali deposit represents generally the resultant from a mixture of salt which has been dissolved and reprecipitated a number of times, and which while dissolved has been seeping through the soil under gravitational forces, or has been moving through the soil as film water under capillary stresses. In either event the salt mixture has been subject to the power for selective absorption peculiar to the particular soil mass through which it has been moving. Re-solution is seldom an instantaneous process, and different rates of solution necessarily involve some separation of salts. Finally the alkali deposit is usually so mixed with other soil material that there cannot be recognized the characteristic solid phases (such, for instance, as the double sulphates of calcium and another base) which serve as guides in laboratory studies and in certain salt mines. Even if the characteristic salts are deposited in surface soils, it is very doubtful, owing to their hygroscopicity, if any but gypsum, halite and Glauber's salt can persist for any length of time. The alternations of temperature from night to day characteristic of arid regions, with precipitation of dews, might easily be expected to make noticeable and rapid changes in the characteristics of any given alkali or salt mixture.

It is not surprising, therefore, that attempts to account for the genesis and present appearance of an alkali deposit by comparison with artificial depositions of salt mixtures, as worked out in the laboratory, have generally been disappointing. On the other hand, laboratory studies have been quite fruitful in elucidating the phenomena taking place on the leaching of alkali from a soil, or so-called "alkali reclamation."

Whatever the origin of the alkali, its segregation at or near the surface of the soil is everywhere much the same; that is, there is a translocation and segregation of soluble salts in the below-surface seepage waters, determined mainly by the topographic features, but partly by the texture and structural properties of the soil and subsoil, with a subsequent rise as capillary water consequent upon evaporation at the surface. Precipitation of the solutes may take place at the surface; more commonly

it takes place a few inches below, owing to the fact that under conditions of rapid evaporation, there is ordinarily a discontinuance in the capillary columns or the film water at a point below the surface of the soil, the water diffusing thence into the above-surface atmosphere as the vapor phase.

The composition of alkali is varied. In the vast majority of cases, the world over, the predominating compound is sodium chloride. When calcium carbonate is a conspicuous component of the soil, as a hard-pan or otherwise, sodium carbonate or black alkali is also generally present, or apt to appear when the land is irrigated. When calcium sulphate or gypsum is likewise present, there is less probability of appreciable amounts of black alkali, and where gypsum predominates or the calcium carbonate is present in relatively inappreciable amounts, black alkali is generally absent, and sodium sulphate is an important constituent of the alkali. Relative rates of diffusion, selective absorption, and sometimes other factors are prominent, however, and the character of the alkali in different spots within a few yards of one another may differ greatly. One of the most interesting manifestations of alkali is the occasional occurrence of a predominating amount of calcium chloride which, as a result of its unusually high hygroscopicity, renders the soil damper, and therefore darker in color than the surrounding soil, and frequently causes even experts to suspect the presence of black alkali. Its true nature can, of course, be determined by a simple chemical examination.

The effect of alkali on the physical properties of the soil is often very marked, aside from the cementing action or hard-pan formation by the carbonate or sulphate of lime. Black alkali, by dissolving and segregating the organic matter at the surface, removes from the lower soil layers the "humus" compounds which are of enormous importance to the maintenance of a soil structure favorable to plant growth. Moreover, black alkali is one of the best of deflocculating agents, and consequently soils where it is a noticeable component, frequently puddle with great readiness and are reclaimed with the utmost difficulty. Most of the other constituents of alkali, however, are flocculat-

ing or "crumbing" agencies, and if not present in too large amounts tend to increase the readiness with which the soil can be brought into good tilth. In this latter case, by separating in the solid phase, or in forming a viscous soil solution, near the saturation point, they sometimes produce a condition in the soil simulating puddling, and where it occurs below the surface, called an alkali hard-pan.

The management of soils infested with alkali is possible in accordance with a few well established principles. Substantial progress has been made in selecting and breeding plants and strains of plants adapted to such soils. Extreme cases are the use of the so-called Australian salt-bushes as forage crops, and the growing of date-palms which through generations of breeding in the oases of the Sahara can thrive in lands so salty as to destroy most of the halophilous plants. More interesting is the unwitting development of the farmers of Utah of strains of wheat and alfalfa which easily withstand three or four times as high a salt content in the soil as do corresponding crops in other alkali regions, such as New Mexico and Arizona.<sup>1</sup> Black alkali, or one in which sodium carbonate is a prominent constituent, is especially destructive to vegetation, not alone on account of a toxic action on plants, but because in any considerable concentration it has a corrosive action on the plant tissue. Not only on this account but also because of its unfortunate effects on the physical properties of the soil, black alkali has received unusual attention from soil investigators. Hilgard<sup>2</sup> has repeatedly urged the use of gypsum as an "antidote" to black alkali, assuming that under conditions of good drainage and aeration a

<sup>1</sup> Some mutual relations between alkali soils and vegetation, by Thomas H. Kearney and Frank K. Cameron, Report No. 71, U. S. Dept. Agriculture, 1902; The date-palm and its utilization in the Southwestern states, by Walter T. Swingle, Bull. 53, Bureau of Plant Industry, U. S. Dept. Agriculture, 1904; The comparative tolerance of various plants for the salts common in alkali soils, by T. H. Kearney and L. L. Harter, Bull. 113, Bureau of Plant Industry, U. S. Dept. Agriculture, 1907; Tolerance of alkali by various cultures, by R. H. Loughridge, Bull. 133, California Agr. Expt. Sta., 1901.

<sup>2</sup> Soils, by E. W. Hilgard, 1906, p. 457-458.

reaction takes place in accordance with the following equation,



Furthermore, it has been shown that calcium salts and especially calcium sulphate exercise a marked ameliorating effect on the action of other salts upon growing vegetation.<sup>1</sup> On the other hand, the reaction indicated by the equation just given does not run to an end with complete precipitation of the carbonate, and the total amount of alkali is increased in the soil by the addition of the gypsum. Unfortunately, Hilgard's suggestion has not yet acquired the sanction of satisfactory field demonstration, although it would seem to merit more consideration than has been given it. Inasmuch as lime is generally a prominent constituent of soils containing black alkali, it is possible that the maintenance of good drainage and aeration in the soil is itself the best corrective of black alkali.

The best use of alkali soils involves irrigation, and it is in the application of irrigation waters that management of alkali soils finds its most highly developed and most important expression. With light sandy soils it has sometimes been found practicable to add sufficient water to carry the alkali down into the soil to such a depth that the crop is well advanced toward maturity before the alkali again rises in sufficient amounts to prove seriously detrimental to the more advanced crops which are generally far more "alkali resistant" than the young seedlings or the germinating seeds. In some cases this procedure can be practiced for a number of years without greatly increasing the seriousness of the alkali conditions, and it may be justified, for a time at least, by economic considerations. Ultimately, however, and more quickly with heavy than with light soils, increasing amounts of alkali must be brought into the surface soil, and this method of irrigating should not be considered as anything more than a temporary expedient. The only procedure which

<sup>1</sup> With the salts occurring in alkali, it is a generality that the effects produced on higher green plants are relatively less with mixtures than with an equivalent amount of a single salt. It has recently been shown, however, that the contrary is true for at least some kinds of bacterial flora. See, On the lack of antagonism between certain salts, by C. B. Lipman, Bot. Gaz., 49, 41-50, (1910).

should be seriously considered as a permanent system on an alkali soil, no matter what the texture, is the installation of underground drains, for which purpose, so far, cylindrical tile drains commend themselves as giving the best results. With a well established system of tile drains, the alkali and all excess of soluble salts can be removed from the soil above the drains; and alkali rising from the soil below can, at least very largely, be prevented from rising to the upper soil layers. The reclamation of an alkali tract by underdrainage is not, however, a necessarily quick operation. Generally it must be a matter of several years persistent and careful effort, but once attained should readily be maintained. The reclamation of an alkali tract by flooding and underdrainage involves the reverse process to the crystallization of salt from a brine. If the water in percolating through the soil were long enough in contact with the salts present to become a saturated solution in equilibrium with them, then the composition of the resulting solution or drainage water would depend upon the particular solid phases or salts which are present in the soil, but not on the amounts of these salts; and the relative proportions of the mineral constituents in the drainage water should remain constant until some one of the solid phases in the soil permanently disappears.

In practice, however, the water passes through the soil at different rates from time to time, the flow from the tiles being copious after a flooding but gradually diminishing as time goes on. One or both of two processes can therefore take place. The water may dissolve some of the salts without at any time or place becoming saturated. As the different salts have different rates of solution as well as different absolute solubilities, it would be expected that not only the concentration of the drainage water, but the composition of the dissolved salts would change from time to time. On the other hand, a part of the water may be imagined to percolate slowly through the finer openings, thus forming a saturated solution with respect to the alkali salts which solution, however, will be diluted on entrance to the drains by a part of the water going through the larger soil openings and dissolving but little salt in its passage. In

this case, it would be anticipated that the concentration of the drainage water would increase as the amount of flow diminished but the composition of the dissolved salts would remain practically constant until some one or more of the alkali salts was completely removed. There are, unfortunately, but few experimental data by which these can be tested. In the accompanying table are given the results of an investigation on the reclamation of an alkali tract near Salt Lake City, Utah, where observations on the composition of the drainage water were made at frequent intervals for more than three years.<sup>1</sup>

At first sight these results might appear to show that the composition of the salts was remaining reasonably constant. This conclusion must be received with caution, however. Variations do occur in the constituents which are present in smaller amount, but the variations are not systematic and may plausibly be explained by dilution of saturated solution by unsaturated solution on entering the drains. Confining attention therefore to the constituents occurring in larger proportions, namely, sodium chloride, sodium sulphate and sodium bicarbonate (including the normal carbonate) it should be remembered that the percentage of sodium in these three salts does not vary much, and the "constancy" may be more apparent than real. Indeed a close inspection of the results indicates that while the sodium is remaining practically unchanged, there is some decrease in the chlorine and a corresponding increase in the sulph-ion. From this it would follow that the sodium chloride was being washed out of the soil more rapidly, proportionately, than sodium sulphate; and it would also appear that the solution entering the drains was not in final equilibrium with the salts in the soil.

How long drainage must continue before there is a radical change in the composition of the seepage water cannot be predicted, and unfortunately data regarding this point are not available. It is certain that in time some one or more of the salts in the soil would be removed and the nature of the drainage

<sup>1</sup> See, Calcium sulphate in aqueous solution, by Frank K. Cameron and James M. Bell, Bull. No. 33, 1906, p. 10 and 70, and Reclamation of alkali land in Salt Lake Valley, Utah, by Clarence W. Dorsey, Bull. No. 43, 1907, p. 13, Bureau of Soils, U. S. Dept. Agriculture.

**COMPOSITION OF THE SALTS IN THE DRAINAGE WATER FROM THE SWAN TRACT, UTAH**

Date	Ca per cent.	Mg per cent.	Na per cent.	K per cent.	SO <sub>4</sub> per cent.	Cl per cent.	HCO <sub>3</sub> per cent.	CO <sub>3</sub> per cent.
ALKALI								
1902—September . . . . .	0.38	0.50	33.74	2.04	18.62	37.76	6.49	0.48
October . . . . .	0.23	0.78	34.73	1.49	19.14	39.52	5.95	0.39
November . . . . .	0.19	0.74	34.42	1.40	18.61	40.46	3.95	0.23
1903—May . . . . .	0.38	0.61	34.48	0.84	29.90	38.19	4.30	0.25
June . . . . .	0.45	0.85	34.18	1.09	17.52	41.04	4.23	0.42
July . . . . .	0.50	0.80	34.06	1.25	18.24	40.24	4.67	0.30
August . . . . .	0.35	0.50	34.40	1.12	17.15	42.37	3.48	0.16
September . . . . .	0.49	0.72	34.54	1.24	17.31	42.02	3.56	0.33
October . . . . .	0.47	1.02	35.43	1.52	16.85	43.26	3.33	0.30
1904—January . . . . .	0.15	0.75	35.93	1.26	20.68	36.64	6.94	0.25
February . . . . .	0.34	0.78	34.59	0.70	18.95	40.15	4.39	—
March . . . . .	0.29	0.77	34.57	1.28	16.31	42.28	3.81	0.19
April . . . . .	0.29	0.70	34.28	1.37	20.93	38.04	5.33	1.46
May . . . . .	0.71	0.74	26.92	4.01	21.16	40.96	4.65	1.38
June . . . . .	0.37	0.70	32.60	3.55	19.94	37.42	4.65	1.57
August . . . . .	0.37	0.56	33.85	2.13	17.12	41.51	5.20	1.16
September . . . . .	0.42	0.79	34.10	1.35	19.01	39.56	4.11	0.37
October . . . . .	1.04	0.60	35.01	1.86	21.42	36.63	4.68	0.76
December . . . . .	1.25	0.70	32.62	1.69	19.89	37.44	6.18	0.22
1905—February . . . . .	0.32	0.67	33.59	0.99	22.30	33.32	8.45	0.36
March . . . . .	0.31	0.66	33.46	1.30	21.60	33.36	8.46	0.35
April . . . . .	0.35	0.65	34.20	1.01	20.03	36.99	6.22	0.55
May . . . . .	0.45	0.86	35.43	1.20	20.59	36.04	6.96	0.47
June . . . . .	0.40	0.94	34.95	1.32	20.89	35.85	5.71	0.84
July . . . . .	0.32	0.69	33.67	1.30	21.17	34.94	7.23	0.68
August . . . . .	0.35	1.04	33.12	1.58	21.58	35.92	5.72	0.99
September . . . . .	0.42	0.82	35.39	1.26	21.18	34.55	7.41	0.67
1906—January . . . . .	0.55	0.84	35.12	1.11	21.10	34.35	8.57	0.36

water would be changed. Alterations in the composition of the drainage water furnish the readiest as well as the best guides as to the changes and the nature of the changes taking place in the soil during the process of reclamation. As a practical matter it should be borne in mind that the persistence of the several salts of the alkali mixture does not mean necessarily that they are evenly distributed in the soil; while yet determining the composition of the water entering the drain, they may have disappeared from the upper soil layers which then may hold a solution of quite different character, suited to the support of crops. In the case just cited the soil contained, before drainage operations were commenced, upwards of 2.7 per cent. of readily soluble salts and would not support any growth other than salt-bushes and similar halophilous plants. Four years later the soil contained less than 0.3 per cent. soluble salts and yielded a very satisfactory crop of alfalfa. In such cases, however, the land cannot be considered as finally reclaimed until a material change in the composition of the drainage water shows that there has been a complete removal of some of the solid salts from that portion of the soil feeding the drains.

The rate at which alkali can be leached from a soil is dependent in a large measure upon the absorptive properties of the soil, and to some extent upon the nature of the salts composing the alkali. The leaching is more rapid from sandy than from clay soils, and white alkali is leached more readily than is black. In general, however, the same laws hold here as in any leaching of a solute from an absorbent, and it has been shown that even in the case of black alkali, the rate of removal under a constant leaching follows the law  $dx/dt = K (A - x)$ .<sup>1</sup> In practice, the water does not percolate through the soil under a constant "head," but the flow is intermittent, so that the value of the above formula is mainly academic. On the other hand, if the drainage between floodings is thorough, this procedure should be more efficient than any other for causing a rapid removal of the alkali salts, if, as is generally the case, a limited quantity of water is available.

<sup>1</sup> The removal of "black alkali" by leaching, by F. K. Cameron and H. E. Patten, Jour. Am. Chem. Soc., 28, 1639. (1906).

Finally, it remains to be pointed out that the use of excessive amounts of water on alkali tracts is quite as unfortunate in its effects as the use of too little. If water be added to an undrained soil or in excess of the capacity of the drains to remove it, incalculable harm may be done by enormously increasing in the surface soil the amount of salts brought up from the lower layers as the capillary stream rises to the surface in consequence of evaporation there. Should the wetting of the soil proceed so far as to establish good capillary connection with the permanent ground water, the harm may be sufficient to offset in a few weeks or months expensive reclamation efforts of years. The harm to the tract where the water is added may be far less than the harm done to other areas. A large proportion of existing alkali deposits or "spots" results from the evaporation of seepage waters coming sometimes from considerable distances. The overwetting of a soil means the production of seepage waters which are to appear at the surface somewhere else, generally at a lower level, and frequently means the more or less complete ruin of the soils of the lower level. The experience of India, Africa and our own arid states in the increase of alkali spots following the introduction of irrigation, added to our present theoretical knowledge, should make the planning of an irrigation project without adequate drainage provisions, a stupidity, and its accomplishment a public crime. Quite as important is the development of a public opinion that the individual cultivator who deliberately or carelessly uses excessive amounts of water on his tract is a serious enemy to the body politic, and should be treated as such.



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